Ferromagnetic Oximate-bridged Complexes of Chromium(III)–Copper(II) and of Chromium(III)–Copper(II)–Chromium(III)

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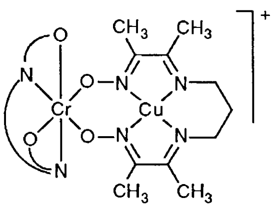
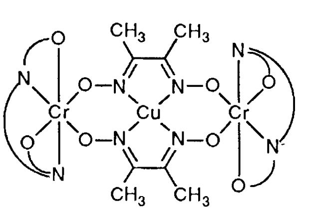
An oximate-bridged binuclear chromium(III)–copper(II) complex [(salen)Cr(pdmg)Cu]ClO$_4$ **1** and a trinuclear chromium(III)–copper(II)–chromium(III) complex [{(salen)Cr}$_2$(dmg)$_2$Cu] **2** have been prepared and characterized [salen^{2-} = *N,N'*-ethylenebis(salicylideneiminate), pdmg^{2-} = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioximate and dmg^{2-} = dimethylglyoximate]. Magnetic susceptibility measurements in the temperature range 4.2–300 K demonstrated the operation of a ferromagnetic interaction between the adjacent chromium(III) and copper(II) ions through oximate bridges in both **1** and **2**. Based on spin Hamiltonians $\mathcal{H} = -2J\hat{S}_1\cdot\hat{S}_2 (S_1 = \frac{3}{2}, S_2 = \frac{1}{2})$ and $\mathcal{H} = -2J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3)$ $(S_1 = S_3 = \frac{3}{2}, S_2 = \frac{1}{2})$, the exchange integrals (J) were evaluated as +12.6 and +13.0 cm^{-1} for **1** and **2**, respectively.

The syntheses and magnetic investigations of ferromagnetic bi- and oligo-nuclear metal complexes have been the subject of many recent studies with the aim of understanding fundamental factors governing the magnetic properties of transition-metal compounds[1,2] and to find appropriate systems applicable as building units for the design of molecular-based ferromagnets.[3] Kahn[1] pointed out two distinct cases that give rise to a ferromagnetic spin coupling between neighbouring paramagnetic metal ions, *i.e.* (*i*) accidental orthogonality and (*ii*) strict orthogonality of magnetic orbitals. The former depends on some structural factors in a subtle manner. This is illustrated by di-μ-hydroxo-dicopper(II) complexes where the magnetic interaction is very sensitive to the Cu–O–Cu angle and changes to ferromagnetism when the angle becomes smaller than 97.7°.[4] It appears that the accidental orthogonality of magnetic orbitals is hardly applied for the design of ferromagnetic complexes because of difficulties in finding the optimum structural conditions for it to occur and, in particular, in materializing such steric conditions in designed metal complexes. The strict orthogonality of magnetic orbitals, on the other hand, can be attained by choosing an appropriate combination of paramagnetic metal ions, and hence the design of ferromagnetic complexes according to this principle seems promising. Thus, we have considered combinations of metal ions and the nature of the bridging systems.[3,5–7] Recent investigations[5,6,8] revealed that a combination of chromium(III) and copper(II) ions can give rise to such strict orthogonality of magnetic orbitals. However, characterized discrete chromium(III)–copper(II) complexes are still few and limited to those bridged by hydroxide,[5] imidazolate,[6] or phenolate[8] groups.

In this study we have synthesised an oximate-bridged binuclear chromium(III)–copper(II) complex [(salen)Cr(pdmg)-Cu]ClO$_4$ 1 and a trinuclear chromium(III)–copper(II)–chromium(III) complex [{(salen)Cr}$_2$(dmg)$_2$Cu] 2, where salen^{2-}, pdmg^{2-} and dmg^{2-} denote *N,N'*-ethylenebis(salicylideneiminate), 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioximate and dimethylglyoximate ions, respectively. The cryomagnetic properties of these complexes have been measured in the temperature range 5–300 K to see the effect of the oximate bridge upon the magnetic interaction between chromium(III) and copper(II) ions.



1



2

Experimental

Physical Measurements.—Elemental analyses for C, H and N were obtained at the Service Centre of Elemental Analysis, Kyushu University. Copper and chromium analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were measured on KBr disks with a JASCO IR-810 spectrophotometer, electronic spectra by the diffuse reflectance technique on a Shimadzu model MPS-2000 multipurpose spectrophotometer. Magnetic susceptibilities were measured with a HOXAN HSM-D SQUID magnetometer in the temperature range 4.2–100 K and with a Faraday balance designed in our laboratory in the range 100–300 K. The apparatus was calibrated with [Ni(en)$_3$]-[S$_2$O$_3$] (en = ethylenediamine).[9] Diamagnetic corrections were made with Pascal's constants.[10] Effective magnetic moments were calculated from the expression $\mu_{eff} = 2.828(\chi_M T)^{\frac{1}{2}}$, where χ_M is the magnetic susceptibility per molecule corrected for diamagnetism of the constituting atoms.

Syntheses.—The starting materials [Cr(salen)(H$_2$O)$_2$]-NO$_3$,[11] [Cu(Hpdmg)]ClO$_4$·H$_2$O,[12] and [Cu(Hdmg)$_2$][13] were prepared by the literature methods.

[(salen)Cr(pdmg)Cu]ClO$_4$ 1. The complex [Cu(Hpdmg)]-ClO$_4$·H$_2$O (210 mg, 0.5 mmol) and triethylamine (1 cm^3) were

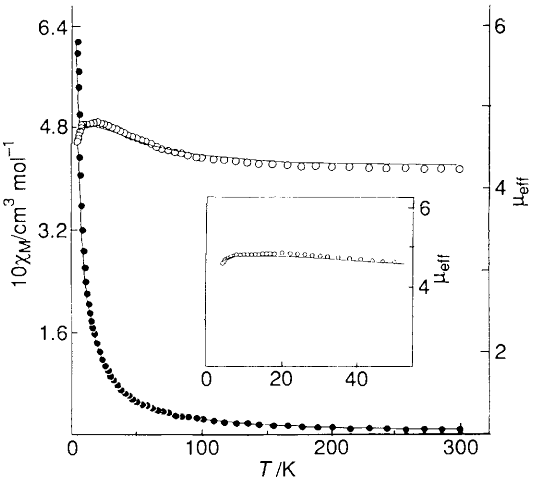


Fig. 1 Temperature dependences of the magnetic susceptibility (●) and effective magnetic moment (○) per molecule for complex **1**. The insert shows an expansion of μ_{eff} *vs.* *T* in the low-temperature range

dissolved in hot absolute ethanol (15 cm^3). To this solution were added $[Cr(salen)(H_2O)_2]NO_3$ (208 mg, 0.5 mmol) and ethyl orthoformate (3 cm^3), and the mixture was refluxed for 1 h to give yellowish brown microcrystals. After the reaction mixture was cooled to room temperature, the crystals were collected, washed with absolute ethanol and dried *in vacuo* over P_2O_5. The yield was 55% (Found: C, 45.10; H, 4.45; Cr, 7.15; Cu, 9.05; N, 11.90. Calc. for $C_{27}H_{32}ClCrCuN_6O_8$: C, 45.05; H, 4.50; Cr, 7.25; Cu, 8.85; N, 11.70%).

$[\{(salen)Cr\}_2(dmg)_2Cu]$ **2**. To a hot absolute ethanol solution (20 cm^3) of $[Cu(Hdmg)_2]$ (147 mg, 0.5 mmol) and triethylamine (2 cm^3) were added a hot absolute ethanol solution (20 cm^3) containing $[Cr(salen)(H_2O)_2]NO_3$ (457 mg, 1.1 mmol) and ethyl orthoformate (3 cm^3), and the mixture was refluxed with stirring. In a few minutes yellow microcrystals were deposited. The reflux was continued for about 2 h. The solution was cooled to room temperature, and the crystals were collected by filtration and dried *in vacuo* over P_2O_5. The yield was 72%. (Found: C, 51.70; H, 4.30; Cr, 10.95; Cu, 6.60; N, 12.00. Calc. for $C_{40}H_{40}Cr_2CuN_8O_8$: C, 51.75; H, 4.35; Cr, 11.20; Cu, 6.85; N, 12.05%).

Results and Discussion

Syntheses and General Characterization.—A promising way to obtain discrete heteronuclear complexes is to use metal complexes which contain potential donor groups for another metal ion.[14–19] In this study we have adopted this strategy to synthesise chromium(III)–copper(II) heteronuclear complexes. For this purpose $[Cu(Hpdmg)]ClO_4$ and $[Cu(Hdmg)_2]$ were chosen, because they can co-ordinate to another metal ion through the deprotonated oximate oxygens to afford bi- and trinuclear complexes doubly bridged by oximate groups.[20–22] As a counter part, $[Cr(salen)(H_2O)_2]^+$ was adopted because this complex reacts with a bidentate ligand (L–L) such as oxalate or acetylacetonate ion to form mixed-chelate complexes $[Cr(salen)(L\text{–}L)]^n$ ($n = -1$ or 0).[11,23] Indeed, the reactions of $[Cr(salen)(H_2O)_2]NO_3$ with $[Cu(Hpdmg)]ClO_4$ (1:1 mole ratio) and with $[Cu(Hdmg)]ClO_4$ (2:1 mole ratio) readily formed $[(salen)Cr(pdmg)Cu]ClO_4$ **1** and $[\{(salen)Cr\}_2(dmg)_2Cu]$ **2**, respectively. They are the first examples of chromium(III)–copper(II) complexes bridged by oximate groups. In spite of our many efforts, single crystals suitable for X-ray crystallography have not yet been obtained for either **1** or **2**.

The starting complexes $[Cu(Hpdmg)]ClO_4$ and $[Cu(Hdmg)_2]$ show an IR band at 2350 and 2600 cm^{-1}, respectively, which may be assigned to the ν(OH) vibration of the hydrogen-bonded N–OH ··· O–N group.[24,25] On the other hand both **1** and **2** show no IR bands in the region 2300–2700 cm^{-1}, indicating that the dioxime protons are fully removed. Each chromium(III) ion must take a *cis*-β octahedral configuration with respect to the tetradentate salen^{2-} ligand as demonstrated for other $[M^{III}(salen)(L\text{–}L)]^n$ complexes (M = Mn, Fe, or Co; $n = -1$ 0, or +1).[26–30] The copper(II) ion probably retains the original planar configuration with four nitrogen donor atoms in each **1** and **2**. The reflectance spectra of **1** and **2** resemble each other and show broad bands at *ca.* 800, *ca.* 600 and *ca.* 500 nm and an intense band at 400 nm. The band at 400 nm is characteristic of the $[Cu(dmg)_2]^{2-}$ and $[Cu(pdmg)]^{2-}$ chromophores with fully deprotonated oximate groups.[21,22]

Magnetic Properties.—The cryomagnetic property of complex **1** is shown in Fig. 1 as plots of μ_{eff} and χ_M *vs.* *T*. The effective magnetic moment per molecule is 4.23 μ_B at room temperature, which is close to the spin-only value (4.24 μ_B) of the magnetically non-interacting chromium(III)–copper(II) system. As the temperature is lowered the magnetic moment increases gradually and reaches a broad maximum 4.81 μ_B at 20 K and then decreases below this temperature to 4.57 μ_B at 4.25 K. The maximum value (4.81 μ_B) is close to the spin-only value 4.90 μ_B for $S = 2$ which corresponds to the highest spin multiplicity derived from the spin coupling between chromium(III) and copper(II). The results clearly indicate the operation of a ferromagnetic spin coupling in this complex. The decrease of μ_B at very low temperature may be attributed to an intermolecular antiferromagnetic interaction. The magnetic susceptibility expression for the $S_1 = \frac{3}{2}$–$S_2 = \frac{1}{2}$ system based on the Heisenberg model $\mathcal{H} = -2J\hat{S}_1\cdot\hat{S}_2$ was derived by Pei *et al.*[31] In the present case the susceptibility expression is modified as in equation (1), introducing a parameter θ to correct for the

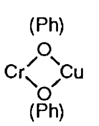
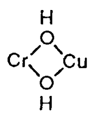
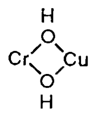
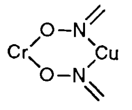
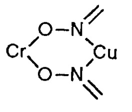
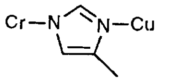
$$\chi_M = \frac{Ng^2\beta^2}{k(T-\theta)} \times \frac{10 + 2\exp(-4J/kT)}{5 + 3\exp(-4J/kT)} + N\alpha \qquad (1)$$

contribution from an intermolecular magnetic interaction. Such a procedure was first adopted by Inoue *et al.*[32] in magnetic analyses of binuclear copper(II) complexes. As indicated by the traces in Fig. 1, a fairly good fitting can be attained with this equation using the magnetic parameters $g = 1.954$, $J = +12.6$ cm^{-1}, $N\alpha = 100 \times 10^{-6}$ cm^3 mol^{-1}, and $\theta = -0.1$ K. The discrepancy factor $\delta = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}]^{\frac{1}{2}}$ was 0.038. The ferromagnetic spin coupling in this complex is weak compared with that in a dihydroxo-bridged complex $[L^1Cr(OH)_2Cu(bipy)_2]$[5] ($J = +25$ cm^{-1}, L^1 = *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, bipy = 2,2′-bipyridyl) and that in the diphenolato-bridged complex $[CuCrL^2(H_2O)_2]Cl$[8] [$J = +52.5$ cm^{-1}, L^2 = *N,N′*-ethylenebis(3-carboxysalicylideneiminate) (4−)].

The cryomagnetic property of complex **2** is shown in Fig. 2. The effective magnetic moment per molecule is 5.86 μ_B at room temperature, which is close to the spin-only value 5.74 μ_B of the magnetically non-interacting trinuclear chromium(III)–copper(II)–chromium(III) system. As the temperature is lowered the magnetic moment increases gradually, reaches a maximum (7.48 μ_B) at 7 K, and then tends to decrease below this temperature. The moment at 4.2 K is 7.24 μ_B. The maximum value 7.48 μ_B at 7 K is slightly smaller than the spin-only value 7.94 μ_B for $S = \frac{7}{2}$ which corresponds to the highest spin multiplicity derived from ferromagnetic spin coupling in the trinuclear $S_1 = \frac{3}{2}$–$S_2 = \frac{1}{2}$–$S_3 = \frac{3}{2}$ system. Nevertheless the magnetic behaviour clearly indicates that a ferromagnetic interaction operates between the chromium(III) and copper(II) ions through the oximate groups. The decrease of the magnetic moment at very low temperature may be attributed to an antiferromagnetic intermolecular interaction.

Based on the spin Hamiltonian $\mathcal{H} = -2\,J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3)$ with $S_1 = S_3 = \frac{3}{2}$ and $S_2 = \frac{1}{2}$ and with Kambe's approach,[33] the low-lying spin states in zero field are obtained as shown in Scheme 1 in which the spin multiplicity of each state is indicated

Table 1 Exchange integrals and intermetal distances of chromium(III)-copper(II) complexes

Complex	Bridging mode	J/cm^{-1}	Ref.	Cr · · · Cu (Å)[a]
$[CuCrL_2(H_2O)_2]Cl$		+52.5	8	(2.97–3.03)
$[L^1Cr(OH)_2Cu(bipy)(CH_3OH)][ClO_4]_3$		(+25)[b]	5	2.987
$[Cu\{(OH)_2CrL^1\}_2][ClO_4]_4$		+40	5	(3.0)
$[(salen)Cr(pdmg)Cu]ClO_4$		+12.6	This work	(3.55–3.75)
$[\{(salen)Cr\}_2(dmg)_2Cu]$		+13.0	This work	(3.55–3.75)
$[(salen)Cr(L^3Cu)_2]ClO_4$		(+8)[c]	6	(6.0–6.3)

[a] Values in parentheses are estimated from related complexes (references being given in the text). [b] Determined on methanol-free samples. [c] Z. J. Zhong, H. Ōkawa, N. Matsumoto, H. Sakiyama and S. Kida, unpublished work.

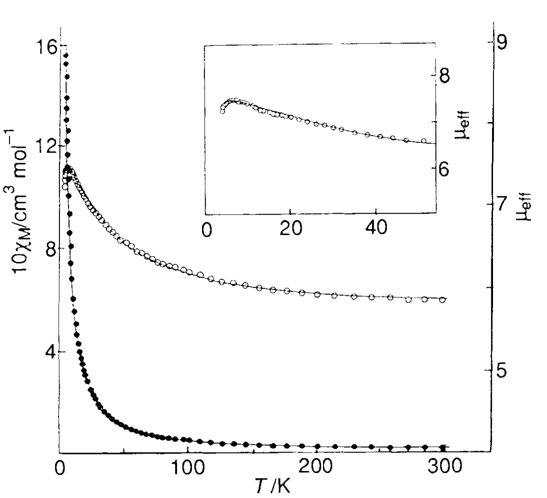
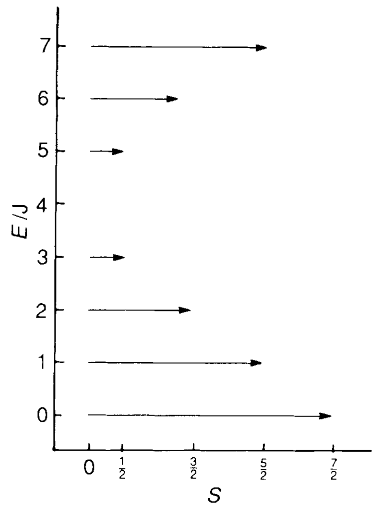


Fig. 2 Temperature dependences of the magnetic susceptibility (●) and effective magnetic moment (○) per molecule for complex **2**. Insert as in Fig. 1



Scheme 1

by an arrow. Scheme 1 illustrates a case of 'irregular spin order', (refs. 1 and 34) which occurs in trinuclear A–B–A complexes with a spin correlation $2S_A > (S_B + \frac{1}{2})$. When the magnetic interaction is ferromagnetic ($J > 0$) the ground spin state is of the largest spin multiplicity $\frac{7}{2}$ ($= 2S_A + S_B$). Upon increasing energy the spin multiplicity of the states first decreases from $\frac{7}{2}$ to

$\frac{1}{2}$ and then increases from $\frac{1}{2}$ to $\frac{5}{2}$. The same order of the spin states has been found for a dihydroxo-bridged chromium(III)–copper(II)–chromium(III) complex $[Cu\{(OH)_2CrL^1\}_2][ClO_4]_4$.[5] The reverse order of the spin states ($J < 0$) has been recognized for trinuclear manganese(II)–copper(II)–manganese(II) and nickel(II)–copper(II)–nickel(II) complexes.[31,34]

The magnetic susceptibility expression for the trinuclear system Cr^{III}–Cu^{II}–Cr^{III} can be derived by the use of Scheme 1 and by applying the Van Vleck equation.[35] In the magnetic analyses the susceptibility equation was modified as in equation (2) by introducing a parameter θ, where $A = 84 + 35\exp(x)$

$$\chi_M = \frac{Ng^2\beta^2}{k(T-\theta)} \times \frac{A}{B} + N\alpha \qquad (2)$$

$+ 10\exp(2x) + \exp(3x) + \exp(5x) + 10\exp(6x) + 35\exp(7x)$, $B = 16 + 12\exp(x) + 8\exp(2x) + 4\exp(3x) + 4\exp(5x) + 8\exp(6x) + 12\exp(7x)$, and $x = -J/kT$.

As shown by the traces in Fig. 2 a good fitting to the experimental data is attained with this equation using magnetic parameters $g = 1.980$, $J = +13$ cm^{-1}, $\theta = -0.5$ K, and $N\alpha = 150 \times 10^{-6}$ cm^3 mol^{-1}. The discrepancy factor was 0.003. The exchange integral (J) is considerably smaller than that of $[Cu\{(OH)_2CrL^1\}_2][ClO_4]_4$[5] ($J = +40$ cm^{-1}). The present study has confirmed that the spin coupling between chromium(III) and copper(II) ions through an oximate group is ferromagnetic.

In Table 1 are summarized the exchange integrals of relevant chromium(III)–copper(II) complexes. Among these complexes only $[L^1Cr(OH)_2Cu(bipy)(CH_3OH)][ClO_4]_3$[5] was structurally analysed, having a Cr···Cu distance of 2.987 Å. A comparable distance (*ca.* 3.0 Å) is estimated for $[Cu\{(OH)_2CrL^1\}_2][ClO_4]_4$. For $[CuCrL^2(H_2O)_2]Cl$ a similar distance (*ca.* 3.0 Å) is also estimated based on X-ray structural data for its Cu^{II}–M^{II} (M = Co, Ni or Mg) analogues.[36–38] The Cr···Cu distance of the present complexes **1** and **2** doubly bridged by oximate groups is estimated at 3.55–3.75 Å based on X-ray structural results for related di- and tri-copper(II) complexes.[20–22] The Cr···Cu distance of the imidazolate-bridged $[(salen)Cr(L^3Cu)_2]ClO_4$ [H_2L^3 = 4-(6-methyl-8-oxo-2,5-diazanona-1,5,7-trienyl)imidazole] is expected to fall in the range 6.0–6.3 Å.[18c,e] The Cr···Cu separations are also included in Table 1. Though our discussions are inevitably restricted only to the Cr···Cu separation because of the lack of detailed structural information, it appears from Table 1 that the intermetal distance is one of the important factors governing ferromagnetic spin coupling between chromium(III) and copper(II) ions. It should be noted that this is not the case for antiferromagnetic spin coupling. For example, complete or nearly complete spin coupling at room temperature has been recognized for some oximate-bridged di- and tri-copper(II) complexes.[20–22,39–41]

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