A Novel Series of Heterotrinuclear Complexes with a Tris(dimethylglyoximato)metal(II) Anion as Bridging Ligand. Structure of the $Fe^{III}Cu^{II}Fe^{III}$ Complex with $S = 9/2$ Ground State

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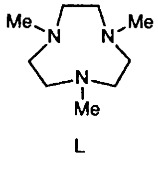
A series of linear heterotrinuclear complexes with a tris(dimethylglyoximato) metal(II) as bridging ligand, $[LFe^{III}\{\mu\text{-}(dmg)_3M^{II}\}Fe^{III}L](ClO_4)_2$ (M = Zn, Cu, Ni, Co, Fe, Mn), where L represents the cyclic triamine 1,4,7-trimethyl-1,4,7-triazacyclononane, has been synthesized and characterized by X-ray crystallography and magnetic susceptibility measurements.

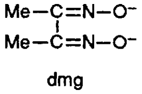
Current research activity concerning the structural and magnetic properties of polynuclear transition metal compounds is aimed at understanding the structural and chemical features governing magnetic exchange coupling through multiatom bridging ligands.[1] Relatively few studies dealing with magnetic trinuclear systems have been reported in comparison to the number of studies dealing with either binuclear or one-dimensional systems. Most of these studies are concerned with homotrinuclear[2] complexes, although a few of them are involved with heterotrinuclear[3] complexes. The heteropolymetallic systems are of interest to both biologists and bioinorganic chemists investigating the structure and function of the polynuclear metal centres in proteins, and physicists or physical inorganic chemists searching for new magnetic materials.

In studying the coordination chemistry of tridentate cyclic amines[4] such as 1,4,7-trimethyl-1,4,7-triazacyclononane (L), we have discovered a general synthetic route for preparing linear heterotrimetallic complexes in which the two terminal metal ions are iron. Herein, we report the synthesis of several linear trinuclear complexes **A** containing two LFe^{III} terminal units and a tris(dimethylglyoximato)metal(II) unit as a bridging ligand. Throughout this paper, the trinuclear complexes are denoted by the respective metal centres only; the terminal and bridging ligands are omitted for simplicity.

$[LFe^{III}\{\mu\text{-}(dmg)_3M^{II}\}Fe^{III}L](ClO_4)_2$
(M^{II} = Zn, Cu, Ni, Co, Fe, Mn)
A



L



$$\begin{array}{l} Me-C{=}N-O^- \\ \quad\;| \\ Me-C{=}N-O^- \end{array}$$

dmg

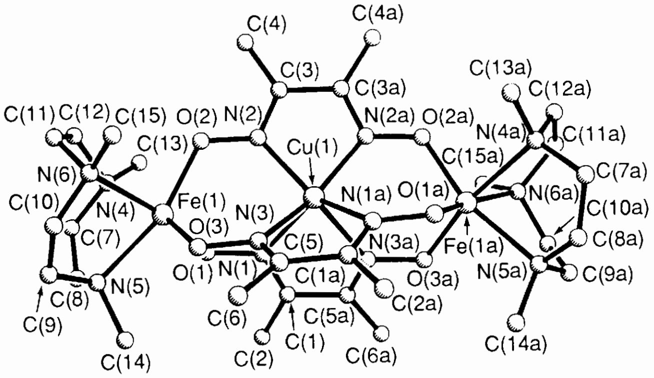


Fig. 1 Structure of the cation in $[L_2Fe_2^{III}\mu(dmg)_3Cu]^{2+}$ in the crystal of $Fe^{III}Cu^{II}Fe^{III}$ complex. Selected bond lengths (Å) and angles (°): Cu(1)-N(1) 2.523(6), Cu(1)-N(2) 2.016(5), Cu(1)-N(3) 1.983(5), Cu(1)-N(1A) 2.069(6), Cu(1)-N(2A) 2.019(5), Cu(1)-N(3A) 2.324(4), Fe(1)-O(1) 1.933(3), Fe(1)-O(2) 1.936(4), Fe(1)-O(3) 1.916(5), Fe(1)-N(4) 2.216(6), Fe(1)-N(5) 2.195(6), Fe(1)-N(6) 2.235(4), N(1)-Cu(1)-N(2) 81.6(2), N(1)-Cu(1)-N(3) 80.5(2), N(1)-Cu(1)-N(1A) 132.2(2), N(1)-Cu(1)-N(2A) 116.8(2), N(1)-Cu(1)-N(3A) 64.1(2), N(2)-Cu(1)-N(3) 96.6(2), N(2)-Cu(1)-N(1A) 143.3(2), N(3)-Cu(1)-N(1A) 79.0(2), N(2)-Cu(1)-N(2A) 77.9(3), N(3)-Cu(1)-N(2A) 160.3(2), N(1A)-Cu(1)-N(2A) 94.1(2), N(2)-Cu(1)-N(3A) 130.5(2), N(3)-Cu(1)-N(3A) 110.6(2), N(1A)-Cu(1)-N(3A) 83.8(2), N(2A)-Cu(1)-N(3A) 86.6(2).

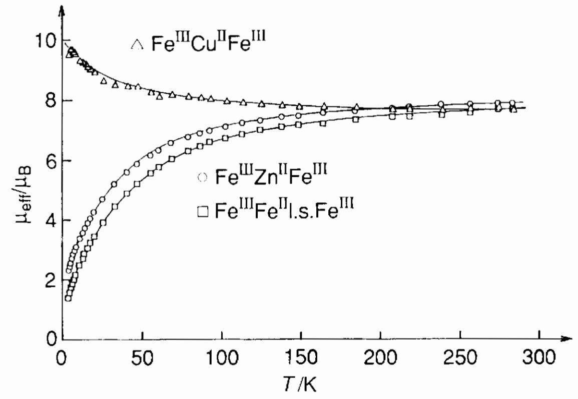


Fig. 2 Plot of μ_{eff} *vs.* T for solid complexes. The solid lines are the theoretical least squares fits to the experimental susceptibility data.

Table 1 Magnetic parameters

Compound	J_{Fe-M}/cm^{-1}	J'_{Fe-Fe}/cm^{-1}	g
$Fe^{III}Zn^{II}Fe^{III}$	—	−3.4(4)	1.98(2)
$Fe^{III}Cu^{II}Fe^{III}$	−42(3)	−3.4(4)	2.00[a]
$Fe^{III}Fe^{II}$l.s.Fe^{III}	—	−4.4(4)	1.98(2)

[a] Kept fixed during fitting procedure.

The $Fe^{III}Cu^{II}Fe^{III}$ complex was synthesized in an argon atmosphere by treating a methanolic solution of the cyclic triamine[5] with sequential additions of $Fe(MeCO_2)_2$ (1 equiv.), $Cu(MeCO_2)_2$ (0.5 equiv.) and dimethylglyoxime (1.5 equiv.) in the presence of triethylamine. The complex was precipitated as the perchlorate salt in the presence of air. The other heterotrimetallic complexes were synthesized by a similar protocol, with all the complexes having satisfactory elemental analysis consistent with the formulation: $[L_2Fe_2^{III}M^{II}(dmg)_3]ClO_4)_2$ (M^{II} = Zn, Ni, Co, Fe, Mn).

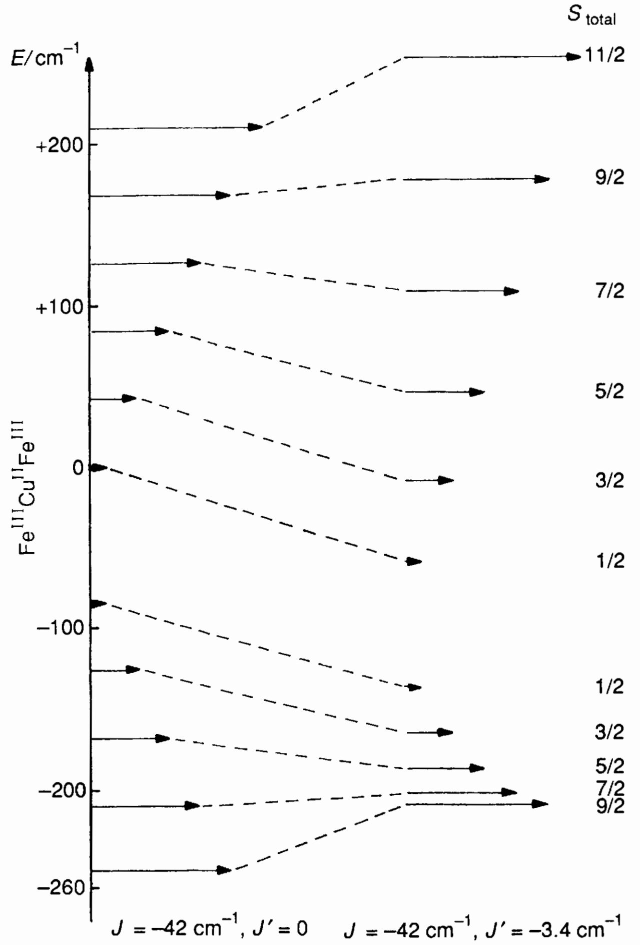


Fig. 3 Energy diagram for the $Fe^{III}Cu^{II}Fe^{III}$ complex

The X-ray structure of $[L_2Fe_2Cu(dmg)_3](ClO_4)_2\cdot 0.5MeOH$ (Fig. 1)† clearly illustrates the trinuclear nature of this complex. The $Cu(dmg)_3^{4-}$ anion bridges the two iron ions through its deprotonated oxime oxygens with a Cu···Fe separation of 3.58 Å. Two facially coordinated tridentate amine ligands complete the trigonally distorted octahedral coordination sphere of the two Fe^{III} centres. The Cu–N distances show that the resultant coordination sphere around the disordered Cu is strongly distorted. The Fe–O and Fe–N distances are consistent with a d^5 high-spin electron configuration of the Fe^{III} centres.

Variable temperature (4.2–284 K) magnetic susceptibility data for crystalline $Fe^{III}Cu^{II}Fe^{III}$, $Fe^{III}Zn^{II}Fe^{III}$ and $Fe^{III}Fe^{II}$l.s.Fe^{III} were fitted by means of least squares to the

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† *Crystal data*: $[C_{30}H_{60}N_{12}O_6Fe_2Cu](ClO_4)_2\cdot 0.5CH_3OH$, monoclinic, *C2/c*, $a = 29.144(5)$, $b = 12.330(3)$, $c = 14.860(2)$ Å, $\beta = 119.22(1)°$, $V = 4660.3$ Å^3, $Z = 4$, $D_c = 1.547$ mg m^{-3}, $F(000) = 2276$, λ(Mo-Kα) = 0.71073 Å, $\mu = 1.26$ mm^{-1}. The structure was determined by direct methods (SHELXTL-PLUS) and refined from 3471 observed reflections [$F > 4\sigma(F)$] measured at room temperature, with anisotropic thermal parameters, and with isotropic H atoms in calculated positions. Disordered Cu was refined with a site occupancy of 0.5 (Split-Model); $R = 0.0602$, $R_w = 0.0574$ for 286 parameters. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1990.

formula for the paramagnetic susceptibility, which results from the spin Hamiltonian (1) for isotropic magnetic exchange

$$\hat{H} = -2J(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_2\cdot\hat{S}_3) - 2J'\hat{S}_1\cdot\hat{S}_3 \quad (1)$$

with $S_1 = S_3 = 5/2$ and $S_2 = 1/2$ or 0. The least-squares fits are shown in Fig. 2. The results are summarized in Table 1. The experimental magnetic moment for $Fe^{III}Cu^{II}Fe^{III}$ increases as the temperature is lowered until a maximum is reached at *ca.* 7 K with $\mu_{eff} = 9.70\ \mu_B$ and $\chi_M\cdot T = 11.75$ cm^3 mol^{-1} K, which is very close to the value of $\chi_M\cdot T = 12.3$ cm^3 mol^{-1} K for $S = 9/2$ ground state. Below 7 K there is a decrease in μ_{eff}, which may be due to the zerofield splitting of the $S = 9/2$ state. A schematic energy ladder is shown in Fig. 3. Thus magnetic interaction between high-spin Fe^{III} and Cu^{II} is antiferromagnetic. For $Fe^{III}Zn^{II}Fe^{III}$ and $Fe^{III}Fe^{II}$l.s.Fe^{III}, magnetic moment decreases steadily with decreasing temperature. Below 80 K μ_{eff} decreases rapidly with decreasing temperature and approaches the value of 2.36 μ_B and 1.42 μ_B at 4.2 K for $Fe^{III}Zn^{II}Fe^{III}$ and $Fe^{III}Fe^{II}$l.s.Fe^{III}, respectively. This magnetic behaviour is typical of antiferromagnetically coupled binuclear paramagnetic centres with a diamagnetic ground state. It is noteworthy that magnetic exchange coupling is observed in these compounds in which the iron^{III} centres are separated by a large distance of *ca.* 7.0 Å, which is definitely not the limit for the intramolecular magnetic interaction.[6]

We have demonstrated a general approach for the rational synthesis of linear heterotrimetallic complexes. The availability of these complexes opens up possibilities for investigating magnetic and electronic interactions between metal centres in a systematic way. Studies focusing on the EPR, Mössbauer and electrochemical properties of these complexes are in progress.

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