

A rational assembly of a series of exchange coupled linear heterotrinnuclear complexes of the type $M_A M_B M_C$ as exemplified by $Fe^{III}Cu^{II}Ni^{II}$, $Fe^{III}Ni^{II}Cu^{II}$ and $Co^{III}Cu^{II}Ni^{II}$

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A general approach for the rational synthesis of linear trinuclear complexes containing three different metals $M_A M_B M_C$ is described and a member of the series, $Fe^{III}Cu^{II}Ni^{II}$, has been characterized by X-ray crystallography and magnetic susceptibility measurements.

This work stems from our interest in using 'metal oximates' as building blocks for synthesizing hetero- and homopolymetallic complexes containing two,¹ three² or four³ metal centres that constitute a common ground for two areas of current interest, molecular magnetism and metal sites in biology. We have previously demonstrated that using our synthetic strategy it is possible to synthesize a series of complexes of the types $M_A M_B M_A$,² $M_A M_B M_B M_A$ ⁴ and $(M_A)_2(\mu_3-O)_2(M_B)_2$.^{3,5} These series are unique and have been proved to be ideal materials for the investigations of exchange mechanism. We describe here a general approach for the rational synthesis of a series of trinuclear complexes containing three different metals $M_A M_B M_C$. To the best of our knowledge these complexes represent the first examples of exchange coupled linear trinuclear complexes containing three different metals. The complexes have been prepared by the general synthetic route shown in Scheme 1. Yields varied between 30% and 50%. Satisfactory analyses (C, H, N, M_A , M_B , M_C) were obtained.

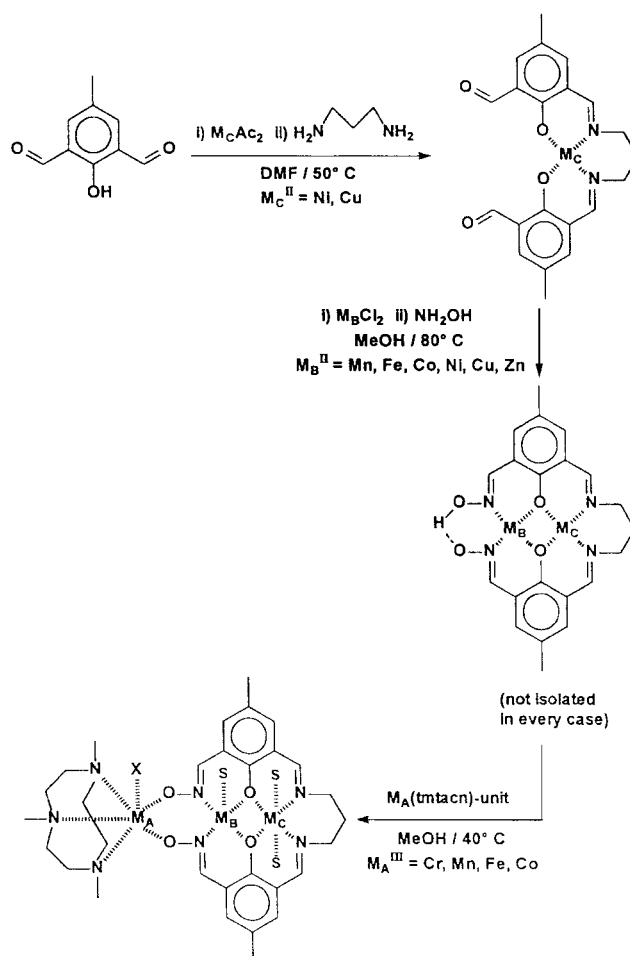
The structure of the complex dication containing the trinuclear core $Fe^{III}Cu^{II}Ni^{II}$, **1**, is shown in Fig. 1.† The coordination geometry of the terminal iron, Fe, is distorted octahedral with three nitrogen atoms, N(1), N(2) and N(3), from the facially coordinated macrocyclic amine, two oxygen atoms, O(1) and O(4), from the oxime ligands and a chloride ion, Cl(1), resulting in the *fac* FeN_3O_2Cl cores. The Fe–O and Fe–N distances are consistent with a d^5 high-spin electron configuration of the Fe centre, as is also evidenced by the Mössbauer spectrum⁶ at 80 K, $\delta = 0.45 \text{ mm s}^{-1}$, $\Delta E_Q = 0.85 \text{ mm s}^{-1}$. The Fe–Cu–Ni skeleton is almost planar, with an angle Fe–Cu–Ni of 174.0° . The intramolecular separations between the metal centres, Fe...Cu 3.695 Å, Fe...Ni 6.772 Å and Cu...Ni 3.087 Å, are in conformity with the values observed earlier for comparable structures.^{2,7} The dihedral angles between the planes FeN(2)N(3)O(1)O(4) and CuN(4)N(7)O(3)O(2), and the latter Cu plane and the Ni plane NiO(3)O(2)N(5)N(6) are 148.5 and 169.4° , respectively.

The geometry of the central Cu(II) centre is square-pyramidal, with the elongated fifth bond (2.43 Å) to axially coordinated oxygen atom O(60) of a methanol molecule. The metrical parameters for the Cu centre are very similar to those of the Cu dimer with the same Schiff-base oxime ligand reported in the literature.⁸

The terminal nickel ion, Ni(II), is coordinated to two azomethine nitrogens, N(5) and N(6), and two bridging phenolate groups, O(2) and O(3), from the Schiff-base oxime ligand. The nickel centre adopts a 6-coordinated environment by interacting with two *trans* axially disposed methanol molecules, O(40) and O(50). The nickel centre is displaced by 0.014 Å from the mean basal plane comprising O(3)O(2)N(5)N(6) atoms toward O(40) or O(50) of a methanol

ligand. The equatorial Ni–N and Ni–O (phenoxide) distances are nearly equal, average 2.005(6) Å and 2.025(3) Å, respectively. The Ni–O(methanol) distances are rather long (av. 2.142 Å), as has been observed earlier.^{9e} The bridging angles Cu–O(2)–Ni and Cu–O(3)–Ni are equal, 101.6° .

Magnetic data (SQUID) with $H = 2 \text{ T}$ for a polycrystalline sample of $FeCuNi$, **1**, are displayed in Fig. 2 as μ_{eff} vs. T . On lowering the temperature μ_{eff} of $6.45 \mu_B$ at 290 K decreases monotonically, approaching a broad minimum around 180 K ($\mu_{\text{eff}} = 6.40 \mu_B$) and increases upon further cooling to reach a maximum with a value of $6.91 \mu_B$ at 15 K, which corresponds to the spin-only value for $S = 3$, expected as the ground state for an antiferromagnetically coupled $Fe^{III}Cu^{II}Ni^{II}$ complex. The μ_{eff} vs. T plot exhibits the expected minimum and indicates an irregular spin-structure^{2,9–11} showing a ferromagnetic-like interaction in the temperature range below this minimum. Below 15 K there is a decrease in μ_{eff} , reaching a value of $4.63 \mu_B$ at



Scheme 1

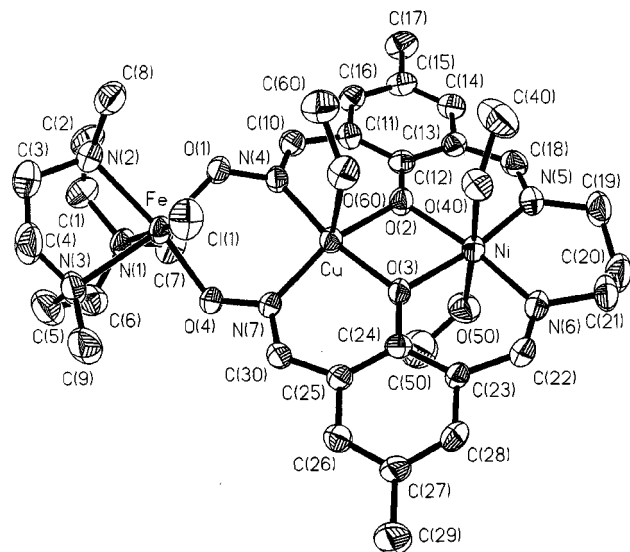


Fig. 1 Structure of the dication $[(\text{tmtacn})\text{Fe}(\text{Cl})\text{Cu}(\text{CH}_3\text{OH})(\text{Schiff-base oxime})\text{Ni}(\text{CH}_3\text{OH})_2]^{2+}$ with the $\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$ core. Selected bond lengths (\AA): Cu–N(4) 1.951(3), Cu–O(3) 1.956(2), Ni–N(5) 2.000(4), Ni–O(2) 2.025(3), Ni–O(50) 2.137(3), Fe–O(4) 1.916(3), Fe–N(1) 2.211(3), Fe–Cl(1) 2.3383(13).

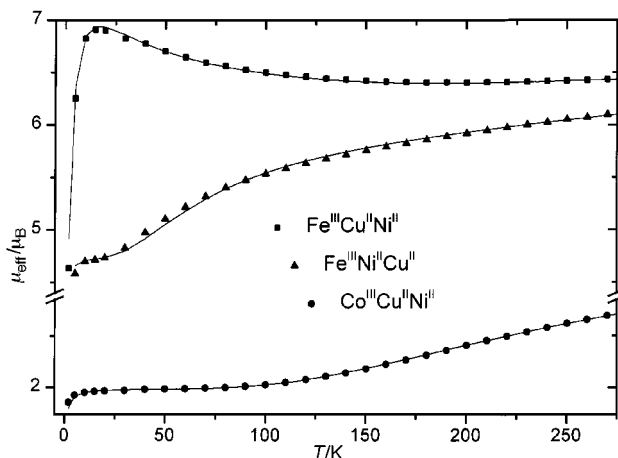


Fig. 2 A plot of μ_{eff} vs. T for **1**, **2**, **3**. The solid lines represent the simulations of the experimental data.

2 K; this behaviour might be due to saturation effects or the splitting in the zero-field of the ground state $S_T = 3$. We have confirmed the ground state of $S_T = 3$ by fitting the experimental magnetization curve (7 T) to the Brillouin function for $S = 3$ with $g = 2.075$ in the temperature range 2–290 K. The magnetic interactions operating in this type of linear trinuclear structure result in a ground state of high-spin multiplicity, although the nearest neighbour spin alignments are antiparallel.

A full-matrix diagonalization approach including exchange ($-2J_1S_1S_2$) and Zeeman interactions, together with axial single-ion zero-field interaction (DS_z^2) for the Ni^{II} ion was employed to fit the experimental data. The best fit shown as the solid line in Fig. 2 yields $J_{\text{FeCu}} = -19.8 \text{ cm}^{-1}$, $J_{\text{CuNi}} = -118.6 \text{ cm}^{-1}$, $J_{\text{FeNi}} = 0$ (fixed), $g_{\text{Ni}} = 2.20$ (fixed), $g_{\text{Cu}} = 2.10$ (fixed), $g_{\text{Fe}} = 2.0$ (fixed), $D = 0$ (fixed).

Our strategy of using ‘building blocks’ sequentially yields also the isomeric $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}$, **2**, as is evident by its susceptibility measurements (Fig. 2). The best fit parameters are $J_{\text{FeNi}} = -10.6 \text{ cm}^{-1}$, $J_{\text{NiCu}} = -161.5 \text{ cm}^{-1}$, $J_{\text{FeCu}} = 0$ (fixed), $g_{\text{Fe}} = 2.0$ (fixed), $g_{\text{Ni}} = 2.30$ (fixed), $g_{\text{Cu}} = 2.10$ (fixed). Thus the exchange interactions in $\text{Fe}^{\text{III}}\text{Ni}^{\text{II}}\text{Cu}^{\text{II}}$, **2**, lead to a different ground state of $S_T = 2$. The exchange interaction between the neighbouring Cu^{II} and Ni^{II} ions in another member of the series, $\text{Co}^{\text{III}}(\text{l.s.})\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$, **3**, also structurally characterized (data not shown), is of comparable strength, $J_{\text{CuNi}} = -125 \text{ cm}^{-1}$ (Fig. 2), to that in **1**, $\text{Fe}^{\text{III}}\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$. The angles Cu–O(phenoxo)–Ni and the distances Cu...Ni are exactly the same in both **1** and **3**, although, in contrast to **1**, the Co–Cu–Ni skeleton is not linear with an angle of 155.6° .

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Notes and references

† $[\text{C}_{33}\text{H}_{53}\text{N}_7\text{O}_8\text{ClFeCuNi}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $M = 1090.3$, monoclinic, space group $P2_1/c$, $a = 14.503(2)$, $b = 16.984(3)$, $c = 19.536(3)$ \AA , $\beta = 106.14(3)^\circ$, $V = 4622.4(13)$ \AA^3 , $Z = 4$, $D_c = 1.567 \text{ g cm}^{-3}$, $T = 293 \text{ K}$, $F(000) = 2256$, $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 1.414 \text{ mm}^{-1}$. Brown black crystal, size $0.40 \times 0.32 \times 0.30 \text{ mm}$, Nonius Kappa CCD, 21617 reflections collected. Structure solution by using the Siemens SHELXTL-PLUS package (G. M. Sheldrick, Universität Göttingen) from 8831 observed reflections; full-matrix least-squares refinement on F^2 , using 7728 reflections and 565 parameters, refinement converged at $R_1 = 0.047$, $R_2 = 0.0895$ (all data). CCDC 182/1032.

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