Magnetic Exchange Coupling in a Nearly Linear Iron(III)Nickel(II)Nickel(II)Iron(III) Complex

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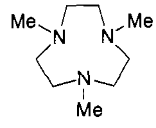
The reaction of $\mathrm{LFe^{III}Cl_3}$ with $\mathrm{Ni_2(Hdfmp)_2}$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane, $\mathrm{H_3dfmp}$ = 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde dioxime) produces in the presence of triethylamine, acetate and tetrafluoroborate ions, the dark brown complex $\mathrm{[L_2Fe_2(\mu_2\text{-}O_2CMe)_2(dfmp)_2(MeOH)_2Ni_2](BF_4)_2}$ which is characterized by X-ray crystallography and magnetic susceptibility measurements and found to have a paramagnetic ground state.

Heteropolymetallic[1–10] systems are of interest to both biologists and bioinorganic chemists investigating the structure and function of polynuclear metal centres in proteins, and to physicists or physical inorganic chemists searching for new magnetic materials.

We have previously utilized 'metal oximates' as bridging ligands to synthesize various homo- and hetero-metal complexes containing two,[11] three[12] or four[13] metal centres. In studying the coordination chemistry of ternary systems containing the tridentate cyclic amine 1,4,7-trimethyl-1,4,7-triazacyclononane (L) and an oxime ($\mathrm{H_3dfmp}$), we envisaged the possibility of preparing a series of linear tetranuclear homo- and hetero-metal complexes of the type $\mathrm{M_AM_BM_BM_A}$. We describe here such a $\mathrm{Fe^{III}Ni^{II}Ni^{II}Fe^{III}}$ tetranuclear species, $\mathrm{[L_2Fe^{III}{}_2(\mu_2\text{-}O_2CMe)_2(dfmp)_2(MeOH)_2Ni^{II}{}_2](BF_4)_2}$, **1**. This has been accomplished by using $\mathrm{Ni_2(Hdfmp)_2}$[14] as a bridging ligand for the $\mathrm{LFe^{III}}$ units.

Complex **1** was synthesized by refluxing a suspension of $\mathrm{LFeCl_3}$ (1 equiv.),[15] $\mathrm{H_3dfmp}$ (1.5 equiv.), $\mathrm{Ni(MeCO_2)_2{\cdot}4H_2O}$ (1 equiv.) and triethylamine (4 equiv.) in methanol (50 $\mathrm{cm^3}$) for 1 h until a dark-coloured solution was obtained. The hot solution was filtered to remove any solid material. Brown crystals† of **1** were obtained as a tetrafluoroborate salt by allowing a solution of tetrabutylammonium tetrafluoroborate in methanol to diffuse through a glass filter into the solution (yield = 23%).‡

The ORTEP plot of the complex cation in **1** containing the tetranuclear $\mathrm{Fe^{III}Ni^{II}Ni^{II}Fe^{III}}$ core along with the atom labelling scheme is shown in Fig. 1(*a*). Fig. 1(*b*) shows only the donor atoms in cation **1**. The Ni(1)O(4)O(4a)Ni(1a) atoms form an exact plane with a centre of inversion. The asymmetric unit thus consists of half of the cation and well separated $\mathrm{BF_4}$ anions. In complex **1**, each nickel ion, Ni(1), is coordinated to two azomethine nitrogens, N(4) and N(5), and two bridging phenolate groups, O(4) and O(4a), from the oxime ligands (dfmp). The nickel centres adopt distorted octahedral environments by interacting with *trans* axially disposed methanol molecules O(5), and acetate ions O(6), that act as bridging ligands O(3), between the iron, Fe(1), and nickel centres, Ni(1). The deviation of the nickel centres toward the methanol molecules from the mean plane of the $\mathrm{N_2O_2}$ (phenoxide) donor sets does not exceed 0.018 Å. The Ni–N equatorial bonds are unequal [Ni(1)–N(5) 2.006(3) and Ni(1)–N(4) 2.031(3) Å]. The Ni(1)–O(5) distance of the coordinated methanol molecule is rather long [2.116(3) Å] as has been observed earlier.[16] The Ni(1)–O(4)(phenoxy) distances are also unequal [2.029(3) and 2.046(3) Å], and lie well within the range of reported values.[17] The two Ni centres are separated by 3.086 Å with a Ni(1)–O(4)–Ni(1a) bridge angle of 98.5(1)°.



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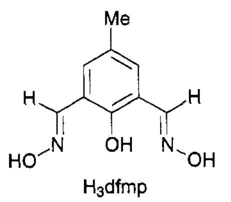


$\mathrm{H_3dfmp}$

The coordination geometry of the terminal iron, Fe(1), is distorted octahedral with three nitrogen atoms, [N(1), N(2) and

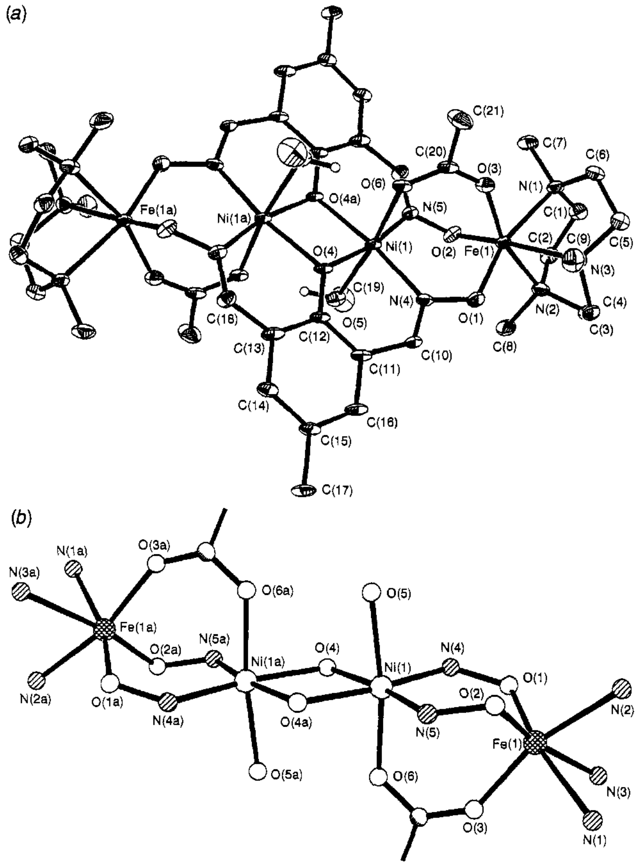


Fig. 1 (*a*) Structure of the cation $\mathrm{[L_2Fe_2(\mu_2\text{-}O_2CMe)_2(dfmp)_2(MeOH)_2Ni_2]^{2+}}$ in **1**. Selected bond lengths (Å) and angles (°): Fe(1)···Ni(1) 3.505, Ni(1)···Ni(1a) 3.086, Fe(1)···Fe(1a) 9.996, Fe(1)–Ni(1)–Ni(1a) 162.5, Ni(1)–O(4) 2.030(3), Ni(1)–O(5) 2.115(3), Ni(1)–O(6) 2.073(3), Ni(1)–N(4) 2.032(3), Ni(1)–N(5) 2.007(3), Ni(1)–O(4a) 2.046(3), Fe(1)–O(1) 1.902(3), Fe(1)–O(2) 1.912(3), Fe(1)–O(3) 1.995(3), Fe(1)–N(1) 2.233(4), Fe(1)–N(2) 2.194(4), Fe(1)–N(3) 2.217(4), O(4a)–Ni(1)–N(5) 88.2(1), O(4a)–Ni(1)–N(4) 169.7(1), O(4a)–Ni(1)–O(6) 87.1(1), O(4a)–Ni(1)–O(5) 87.2(1), O(4a)–Ni(1)–O(4) 81.6(1), N(5)–Ni(1)–N(4) 102.0(1), N(5)– Ni(1)–O(6) 89.5(1), N(5)–Ni(1)–O(5) 96.5(1), N(5)–Ni(1)–O(4) 169.7(1), N(4)–Ni(1)–O(6) 94.4(1), N(4)–Ni(1)–O(5) 90.1(1), N(4)–Ni(1)–O(4) 88.2(1), O(6)–Ni(1)–O(5) 171.7(1), O(6)–Ni(1)–O(4) 89.1(1), O(5)–Ni(1)–O(4) 84.0(1), N(3)–Fe(1)–N(2) 79.9(1), N(3)–Fe(1)–N(1) 78.9(1), N(3)–Fe(1)–O(3) 92.1(1), N(3)–Fe(1)–O(2) 166.3(1), N(3)–Fe(1)–O(1) 85.8(1), N(2)–Fe(1)–N(1) 79.8(1), N(2)–Fe(1)–O(3) 164.9(1), N(2)–Fe(1)–O(2) 86.9(1), N(2)–Fe(1)–O(1) 93.3(1), N(1)– Fe(1)–O(3) 86.2(1), N(1)–Fe(1)–O(2) 95.3(1), N(1)–Fe(1)–O(1) 164.0(1), O(3)–Fe(1)–O(2) 99.9(1), O(3)–Fe(1)–O(1) 98.9(1), O(2)–Fe(1)–O(1) 98.7(1); (*b*) a view of the first coordination spheres of the metal ions in **1**.

N(3)], from the facially coordinated tridentate macrocyclic amine (L) and three oxygen atoms [O(1) and O(2) from the oxime ligands, dfmp, and O(3) from the bridging acetate], resulting in *fac*-FeN_3O_3 cores. The terminal Fe(1) is displaced by 0.074 Å from the mean basal plane comprising N(1)N(3)O(1)O(2) atoms toward the apical nitrogen atom N(2) of the macrocyclic amine. The Fe–O and Fe–N distances are consistent with a d^5 high-spin electron configuration of the Fe-centres.[15] The Fe–Ni–Ni–Fe skeleton is not perfectly linear; the angle Fe(1)–Ni(1)–Ni(1a) is 162.5°. An intramolecular separation between the terminal iron ions, Fe(1)···Fe(1a), of 9.996 Å is found. The Fe(1)···Ni(1) distance, 3.505 Å, is in conformity with a similar value observed earlier.[12c] The dihedral angle between the plane N(1)N(3)O(1)O(2) containing the Fe^{III} ion and the plane N(4)N(5)O(4)O(4a) containing the Ni^{II} ion is 46.8°.

Magnetic data (SQUID) for a polycrystalline sample of **1** were collected in the temperature range 2.0–300.3 K and are displayed in Fig. 2. The molar paramagnetic susceptibility increases continuously with decreasing temperature from 0.032 emu (μ_{eff} = 8.77 μ_B) at 300.3 K to 0.265 emu (μ = 2.05 μ_B) at 2.0 K. The μ_{eff} value of 8.77 μ_B is much lower than the value μ_{eff} = 9.28 μ_B expected for non-interacting two spins of 5/2 and two spins of 1 with an average g = 2.0. Thus the magnetic interaction prevailing in **1** is antiferromagnetic in nature. The data also clearly indicate that this complex does not possess a well separated $S_T = 0$ ground state. In a qualitative sense the $S_T = 0$ state can be thought of in terms of an antiferromagnetic coupling of the two high-spin Fe^{III} ($S_{Fe} = 5/2$) and two high-spin Ni^{II} ($S_{Ni} = 1$) ions to create a ground state of zero net spin.

The magnetic analysis was carried out using the model shown in Scheme 1. In this model J_{ik} represents the exchange interaction between the *i*th and *k*th paramagnetic ions; thus $J_{12} = J_{34}$ describes the interaction between the adjacent iron and nickel ions, J_{23} the interaction between the neighbouring nickel ions, and J_{14} the interaction between the terminal iron ions. A full-matrix diagonalization approach including magnetic exchange ($-2J\vec{S}\cdot\vec{S}_B$), Zeeman interactions and axial single-ion zero-field interaction ($D\hat{S}_z^2$) for the Ni^{II} ion, was employed to fit the data. The preliminary best fit shown as solid lines in Fig. 2 yields $J_{12} = J_{34} = -6.8$, $J_{13} = J_{24} = -3.2$, $J_{23} = -7.7$, $J_{14} = -1.8$ cm^{-1}, and $D_{Ni} = -3.90$ cm^{-1} ($g_{Ni} = 2.21$, $g_{Fe} = 2.00$ and $D_{Fe} = 0.0$ kept fixed). The Zeeman interaction of the high-spin ferric ion in the $^6A_1$ ground state with practically no contribution from the orbital angular momentum is isotropic and the observed g_{Fe} values[18] are very close to the free-electron spin value of 2.00. The above solution is not unique in the sense that a similarly good fit can be obtained with D_{Ni} being constrained to zero, and $g_{Fe} = 2.00$ and $g_{Ni} = 2.17$(fixed) during the fitting procedure: $J_{12} = J_{34} = -7.4$, $J_{13} = J_{24} = -2.9$, $J_{23} = -8.4$ and $J_{14} = -1.6$ cm^{-1}. A comparison of the parameter sets demonstrates the covariance of D and g values, together with small variations in J values. We discarded the second solution, because for the octahedral Ni^{II} a zero-field splitting has to be expected and the g_{Ni} value of 2.21 of the first solution lie well within the range of 2.1–2.3, as described in the literature.[17,19] Furthermore, without zero-field splitting D_{Ni} the low-temperature susceptibilities can not be satisfactorily reproduced, because the fit leads to a ground state $S_T = 0$ with a close lying first excited state $S_T = 1$ at 2.7 cm^{-1}. On the other hand, zero-field interaction splits and severely mixes the spin multiplets, due to substantial competition of zero-field and exchange interaction. As a result, especially with $D_{Ni} < 0$, the ground state is a magnetic sublevel which for arbitrary orientations of the field exhibits a spin expectation value and contributes to the magnetization of the sample. Further measurements and analyses of low-temperature field-dependences at $T < 4.2$ K will be necessary for full clarification and will be subject of a future paper, in conjunction with EPR and Mössbauer investigations.

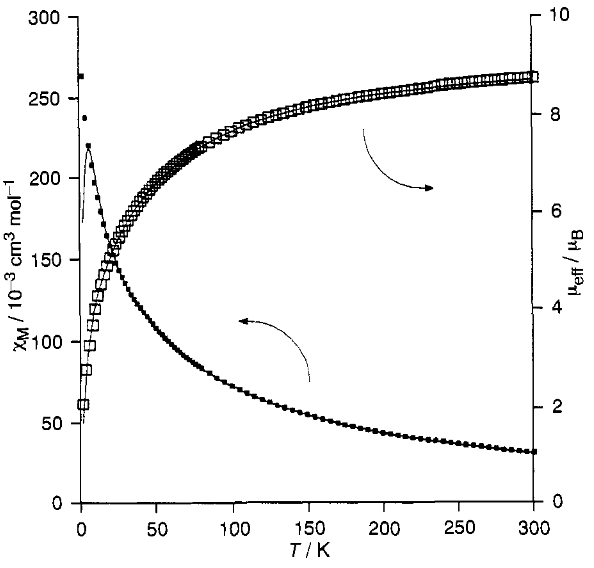
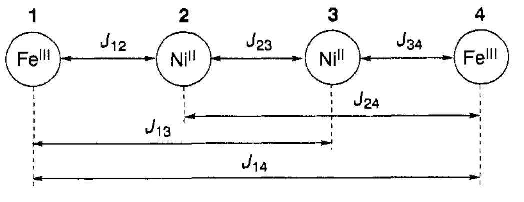


Fig. 2 Plots of χ_M and μ_B *vs.* T for **1**. The solid lines represent the best least-squares fit of the experimental data to the theoretical equation.



Scheme 1

The evaluated value of the zero-field splitting parameter D_{Ni} is in full conformity with the non-zero magnetic moment of 2.05 μ_B at 2.0 K, which indicates that **1** has an extremely complicated low-lying magnetic structure with a non-diamagnetic ground state, which is not well separated from the upper-lying states (although it should be added that fitting of the susceptibility data does not provide the most accurate means of determining D values). It is worth noting that the exchange interaction between the neighbouring Fe^{III} and Ni^{II} ions, $J_{12} = -6.8$ cm^{-1}, for **1** is appreciably weaker than that in a similar oximato-bridged trinuclear $Fe^{III}Ni^{II}Fe^{III}$-complex[12c] ($J = -32$ cm^{-1}), although the Fe···Ni separations are the same, 3.50 Å. Considering the Fe···Fe separation of 10 Å, the superexchange interaction between the terminal ferric centres is appreciable. The spin coupling between the adjacent nickel centres, $J_{23} = -7.7$ cm^{-1}, is not strong, as has been observed earlier.[17] Recently a linear dependence of J on the Ni–O–Ni bridge angles in phenoxy-bridged dinickel(II) complexes has been found by Nag and coworkers.[20] The complex **1** with a Ni–O(4)–Ni angle of 98.5° also fits well to this magnetostructural correlation. A more detailed analysis of the magnetic parameters will be the subject of a future paper.

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Footnotes

† *Crystal data* for **1**: $C_{42}H_{70}B_2F_8Fe_2N_{10}O_{12}$, triclinic, space group $P\bar{1}$ (no. 2), a = 8.537(2), b = 9.852(2), c = 18.000(2) Å, α = 101.63(1), β = 93.31(1), γ = 107.22(2)°, V = 1405.2 Å^3, Z = 1, D_c = 1.55 g cm^{-3}, T = −175 °C, $F(000)$ = 678, λ(Mo-Kα) = 0.71069 Å, μ = 12.57 cm^{-1}. Brown–black crystal, 0.35 × 0.53 × 0.53 mm, Enraf–Nonius CAD 4 diffractometer, graphite monochromator, lattice parameters refined from 25 reflections $22.37 \leqslant 2\theta \leqslant 47.11°$; ω–2θ scan, 6777 intensities collected, no

absorption correction, structure solution (SHELXL-86) and refinement (SHELXL-93) from 5019 observed reflections [$F > 4\sigma(F)$] measured at -175 °C; full-matrix least-squares refinement based on 434 parameters, refinement converged at $R = 0.079$, $R_w = 0.172$ (all data).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallogrpahic Data Centre. See Information for Authors, Issue No. 1.

‡ Satisfactory analyses (C, H, N, Fe and Ni) were obtained.

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