Rational design of azide-bridged bimetallic complexes. Crystal structure and magnetic properties of $Fe^{III}MFe^{III}$ ($M = Ni^{II}$ and Cu^{II}) trinuclear species

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Received (in Cambridge, UK) 2nd September 2004, Accepted 20th October 2004
First published as an Advance Article on the web 2nd December 2004
DOI: 10.1039/b413433h

The first examples of azide-bridged bimetallic trinuclear complexes $\{[M(cyclam)][FeL(N_3)(\mu_{1,5}\text{-}N_3)]_2\}$ (H_2L = 4,5-dichloro-1,2-bis(pyridine-2-carboxamido) benzene) have been structurally and magnetically characterized.

The azide anion is a versatile ligand that is able to link metals ions with different coordination modes, generating a wide variety of azide-bridged polynuclear complexes with intriguing structures (spanning from discrete molecules to 3D arrays) and interesting magnetic properties (antiferromagnetic, ferromagnetic, regular and irregular alternating and canted systems).[1] The most common bridging coordination modes of the azide ligand are end-on (EO) and end-to-end (EE), which generally mediate ferro- and antiferromagnetic exchange interactions, respectively.[1a] In spite of the great versatility of the azide ligand, to our knowledge, no examples of genuine azide-bridged heterometallic complexes have been reported to date. We report here the first examples of such compounds.

The most successful synthetic strategy for heterometallic complexes is the use of metal complexes as ligands, that is to say, metal complexes containing potential donor atoms for another metal ion or metal complex with empty or available coordination sites. We have followed this strategy in an attempt to obtain bimetallic complexes, in which the azide ligand bridges two different metal ions. For this, the azide containing mononuclear anion $[Fe(L)(N_3)_2]^-$ (H_2L = 4,5-dichloro-1,2-bis(pyridine-2-carboxamido) benzene), prepared *in situ* from the reaction of $[Fe(L)Cl(H_2O)]\cdot H_2O$[2] and NaN_3, has been used toward highly thermodynamically stable $[M(cyclam)]^{2+}$ (M = Cu(II) and Ni(II); cyclam = 1,4,8,11-tetraazacyclotetradecane) macrocyclic complexes. The assembly of these two building blocks led to the formation of two azide-bridged heterotrinuclear complexes $\{[M(cyclam)][Fe(L)(N_3)(\mu\text{-}_{1,5}\text{-}N_3)]_2\}$ (M = Ni(II) **1** and Cu(II) **2**).† These trinuclear complexes are of additional interest because they exhibit an irregular spin state structure,[3] in the sense that the spin of the low-lying states does not vary linearly with the energy, but first it decreases and then increases. Consequently, for $J < 0$, the $\chi_M T$ plot is expected to exhibit a minimum. Although numerous examples of well structurally and magnetically characterized bimetallic trinuclear complexes have been reported to date, only a few of them exhibit irregular spin state structure.[4] Moreover, as far as we know, all these systems contain either bis(oxamato)[4a–c] or oxalato[4d] or dimethylglyoximato[4e–f] anions as bridging ligands. Among them, there exist only one example of each of the $Fe^{III}NiFe^{III}$ and $Fe^{III}CuFe^{III}$ type complexes, both having the same basic structure $[LFe\{(\mu\text{-dmg})_3M\}FeL\}X_2$ ($M = Ni^{II}$, $X = PF_6^-$; $M = Cu^{II}$, $X = ClO_4^-$)[4f]

The structures‡ of **1** and **2** are very similar and consist of discrete trinuclear $\{[M(cyclam)][Fe(L)(N_3)(\mu_{1,5}\text{-}N_3)]_2\}$ molecules with C_i symmetry, in which two $[Fe(L)(N_3)_2]^-$ anions are coordinated through single EE azide bridging ligands to the central M(cyclam) unit in trans positions, leading to a linear conformation with Fe–Ni and Fe–Cu distances of 5.63(1) and 5.67 (1) Å, respectively (Fig. 1).

The central atom (Cu^{II} or Ni^{II}) lies on a centre of symmetry and exhibit a MN_6 axially distorted geometry with N–M–N *cis* angles in the ranges 84,4(2)–95.6(2) and 81.9(9)–98.1(9)°, for **1** and **2**, respectively. In this description the four nitrogen atoms of the cyclam ligand occupy the equatorial positions with M–N distances of about 2 Å, whereas two nitrogen atoms belonging to the azide-bridging ligands are located in axial positions with Ni–N7 and Cu–N7 distances of 2.218(5) and 2.548(6) Å for **1** and **2**, respectively. The longer distance for **2** is due to the Jahn–Teller effect involving the Cu^{II} ion. As usual, the end-to-end azido bridge shows asymmetric coordination with Ni–N7–N6 and Fe–N5–N6 angles of 130.8(4) and 123.5(4)°, respectively, for **1** and Cu–N6–N7 and Fe–N6–N5 angles of 119.2(2) and 121.9(2)°, respectively, for **2**. The τ torsion angle defined as the dihedral angle between M–N6–N7–N5 and Fe–N6–N5–N7 mean planes is 78.2(2)° for **1** and 105.6 (4)° for **2**. Fe^{III} ions exhibit distorted octahedral geometry, in which the four nitrogen atoms of the L^{2-} ligand occupy the equatorial positions, whereas the nitrogen atoms N5 and N10 of

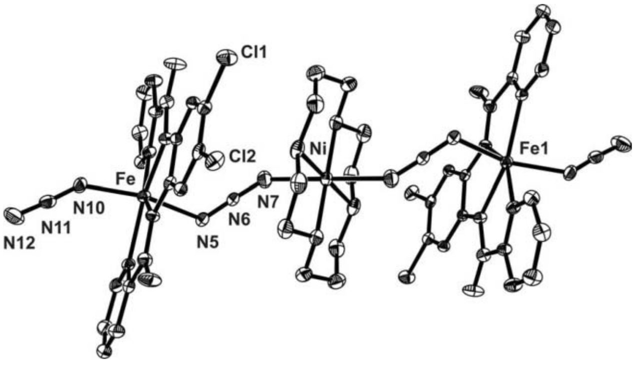

Fig. 1 The molecular structure of **1** (shown) and **2**; H atoms omitted for clarity.

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the bridging and terminal azide groups are located in the axial positions. Bond distances and angles involving the $[Fe(L)(N_3)_2]$ unit agree well with those reported for other compounds containing octahedral $[Fe(L)(N_3)_2]^-$ anions. The equatorial coordination planes for the Fe^{III} ions are parallel but the dihedral angles between the Fe^{III} and M^{II} equatorial coordination mean planes for Fe^{III} and M are 134.9(4) and 46.7(2)°, respectively. The trinuclear molecules are well isolated in the structure; the shortest intermolecular metal–metal distance being of 7.525 and 7.514 Å for **1** and **2**, respectively.

The magnetic susceptibility data for polycrystalline samples of **1** and **2** were measured in the temperature range 2–300 K (Fig. 2). At room temperature, the $\chi_M T$ product (χ_M is the magnetic susceptibility per Fe_2M trinuclear molecule) for **1** is 10.14 $cm^3\ mol^{-1}$ K, which is very close to the calculated value, 9.75 for an uncoupled system with two high-spin Fe^{III} ions ($S = 5/2$) and one Ni^{II} ion ($S = 1$), assuming an average $g = 2.0$. Upon cooling, $\chi_M T$ decreases monotonically and reaches a minimum at 25 K with a value of 8.37, then increases to maximum at 6 K ($\chi_M T = 9.06$) and finally decreases sharply to a value of 7.37 $cm^3\ mol^{-1}$ K at 2 K. This behaviour agrees well with that expected for an antiferromagnetic coupling between the central Ni^{II} ion and the terminal Fe^{III} ions, leading to an irregular spin state structure with zero-field splitting of the ground state $2S_{Fe}\text{-}S_{Ni} = 4$. The reduced molar magnetisation ($M/N\beta$) at 2 K and 5 T (the maximum applied field) is 7.7 $N\beta$, very close to the expected saturation value of 8 $N\beta$ for an $S = 4$ ground state (with $g = 2.0$), which is in agreement with the observed antiferromagnetic coupling.

For **2**, the $\chi_M T$ value at room temperature, 9.27 $cm^3\ mol^{-1}$ K, is close to the spin-only value of 9.125 $cm^3\ mol^{-1}$ K with average $g = 2.0$. As the temperature is lowered, $\chi_M T$ remains almost constant until around 100 K, then increases to reach a maximum with a value of 10.40 at 5 K and finally decreases sharply to 9.24 $cm^3\ mol^{-1}$ K upon cooling down to 2 K. Such a magnetic behaviour is consistent with a ferromagnetic coupling between the central Cu^{II} ion and the terminal Fe^{III} ions with zero-field splitting of the $S = 11/2$ ground state. Although the spin state structure for **2** is also irregular, the $\chi_M T$ *vs.* T plot does not show any minimum because $J > 0$. The value of reduced magnetisation for 2 at 2 K and 5 T is 9.23 $N\beta$, which is intermediate between the expected values for $S = 9/2$ (antiferromagnetic coupling) and $S = 11/2$ (ferromagnetic coupling) ground states. The fact that the value is higher than that for a $S = 9/2$ ground state at 5 T, where the compound is not yet saturated, seems to support the observed ferromagnetic coupling. A full-matrix diagonalisation approach[5] including spin exchange ($-J(S_{Fe1}\cdot S_M + S_{Fe2}\cdot S_M)$), Zeeman and single ion zero-field interactions (DS_z^2) has been employed to analyze the data. The remote coupling constant J_{FeFe} between terminal Fe^{III} ions, which are separated by a distance higher than 11 Å, was assumed to be zero in both compounds. The best parameters obtained with this computing model are: $J_{FeNi} = -6.20\ cm^{-1}$, $D_{Fe} = 2.58\ cm^{-1}$, $D_{Ni} = -4.70\ cm^{-1}$ and $g_{av} = 2.065$ ($R = 1.03 \times 10^{-4}$) for **1** and $J_{FeCu} = 2.06\ cm^{-1}$, $D_{Fe} = 4.6\ cm^{-1}$ and $g_{av} = 2.008$ ($R = 1.8 \times 10^{-4}$) for **2**. As it is difficult to unambiguously determine the sign of D from powder magnetic susceptibility data,[6] one should not put much weight on the absolute value of D parameters. For **1** the $S = 4$ ground state lies 6.20 cm^{-1} below the first excited state with $S = 3$, whereas for **2** the $S = 11/2$ ground state lies 1.03 cm^{-1} below the first excited state with $S = 9/2$. According to MO-Extended Hückel calculations and experimental results for EE homonuclear complexes,[7] the strongest antiferromagnetic coupling is expected for M–N–N angles close to 110°. Moreover, for a given M–N–N angle, the antiferromagnetic coupling decreases as τ increases. In **1**, the d_{z^2} magnetic orbitals of the Ni(II) and Fe(III) ions, which point out to the end nitrogen atoms of the azide bridging ligand, are well oriented to overlap and then to give rise to antiferromagnetic exchange interactions. In keeping with this and with the relatively low M–N–N angles and a high τ angle, weak to medium antiferromagnetic interactions are expected, in good agreement with the experimental data. In **2**, the magnetic orbital of the copper(II) atom is of the type $d_{x^2-y^2}$ (the x and y axes being defined by the short Cu–N(cyclam) bonds) with a very low spin density on the axial positions (z axis), which are filled by the N atoms of the azide-bridging ligands. This leads to a negligible overlap ($J_{AF} \approx 0$) and, if exist, to a weak ferromagnetic interaction ($J \approx J_F$). The large $Cu\text{–}N_{azide}$ distance of 2.548 Å also accounts for the weakness of the magnetic coupling observed.

We are currently investigating the reaction of $[M(L)(N_3)_2]^-$ ($M = Cr^{III}$, Mn^{III} and Fe^{III}) anions towards metal ions and metal complexes not only to obtain heterotrinuclear azide-bridged systems but also extended networks.

This work was supported by the Spanish Ministry of Science and Education (Project BQU2001-3221) and the Junta de Andalucia; I. B. M. thanks the Spanish Agency of International Cooperation (AECI) for a predoctoral grant.

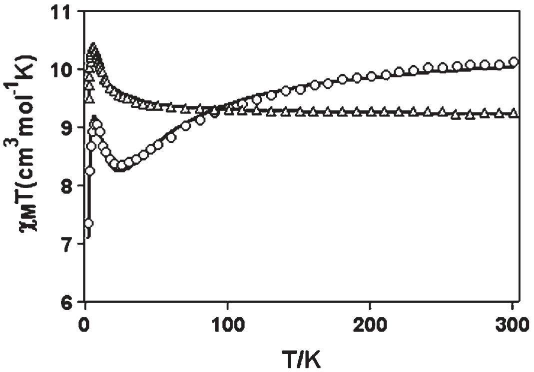

Fig. 2 Temperature dependence of $\chi_M T$ for **1** (circles) and **2** (triangles). Solid lines represent the best data fit.

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Notes and references

† Complex **1** was prepared as follows: A methanol suspension (50 ml) of $[Fe(L)Cl(H_2O)]\cdot H_2O$ (39.6 mg, 0.08 mmol) and NaN_3 (10.4 mg, 0.16 mmol) was heated and stirred until the appearance of a clear green solution. The solution was then filtered to remove any insoluble material. A methanol solution (40 ml) of $[Ni(cyclam)(ClO_4)_2]$ (18.3 mg, 0.04 mmol) was slowly

added to the filtrate, after which the mixture was boiled for 15 min. After filtering and slow evaporation at room temperature of the resulting solution for two days, black crystals were obtained. Yield: 15% based on nickel; IR (KBr), ν(N–N–N), 2060 cm^{-1}. Dark-green crystals of compound **2** were prepared by using the same method as for **1**, after evaporation of the resulting solution for one day. Yield 50%; IR (KBr), ν(N–N–N) 2059 cm^{-1}. Elemental analyses are in agreement with their formulae.

‡ Crystal and structure refinement parameters for **1** and **2**. Complex **1**: $C_{46}H_{44}N_{24}O_4Cl_4Fe_2Ni$, M = 1309,26, monoclinic, space group $P2_1/c$, a = 9.787(3), b = 13.274(4), c = 20.682(6) Å, β = 95.242(7)°, V = 2675.5(13) $Å^3$, Z = 2, D_c = 1.625 g cm^{-3}, μ(Mo-Kα) = 1.153 mm^{-1}, T = 293 K, F(000) = 1336, $R1$ = 0.0757 ($wR2$ = 0.1256) for 6070 unique reflections (R_{int} = 0.088) with a goodness-of-fit of 0.986. Compound **2**: $C_{23}H_{22}N_{12}O_2Cl_2FeCu_{0.5}$, M = 675.05, monoclinic, space group $P2_1/c$, a = 9.8154(9), b = 13.1970(12), c = 20.7739(19) Å, β = 95.782(2)°, V = 2677.2(4) $Å^3$, Z = 4, D_c = 1.630 g cm^{-3}, μ(Mo-Kα) = 1.197 mm^{-1}, T = 298(2) K, F(000) = 1338, $R1$ = 0.0380 ($wR2$ = 0.0946) for 6108 unique reflections (R_{int} = 0.023) with a goodness-of-fit of 1.024. Data were collected by $\omega/2\theta$ ($2\theta_{max}$ = 56°) on a Bruker SMART CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined on F^2 by the SHELX-97 program. CCDC 249654 and 249655. See http://www.rsc.org/suppdata/cc/b4/b413433h/ for crystallographic data in .cif or other electronic format.

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