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Synthesis, crystal structure and magnetic properties of a new cyanide-bridged iron(III)–nickel(II) ferromagnetic chain

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ABSTRACT

The reaction of the iron(III) unit *fac*-[Fe{HB(pz)$_3$}(CN)$_3$]$^-$ [HB(pz)$_3^-$ = hydrotris(1 − pyrazolyl)borate] as the lithium salt (**1**) with the nickel(II) complex *mer*-[Ni(dpt)(H$_2$O)$_3$](ClO$_4$)$_2$ [dpt = dipropylenetriamine] in water affords the heterometallic compound of formula {[Fe^{III}{HB(pz)$_3$}(CN)$_3$]$_2$[Ni^{II}(dpt)]}$_n \cdot 3n$H$_2$O (**2**). The structure of **2** has been determined by X-ray diffraction on single crystals and their magnetic properties have been investigated in the temperature range 1.9–300 K. Compound **2** is a zigzag chain compound with regular alternating bis-monodentate [Fe(1){HB(pz)$_3$}(CN)$_3$]$^-$ units and [Ni(dpt)]$^{2+}$ cations, the six coordination around the nickel atom being achieved by the coordination of another [Fe(2){HB(pz)$_3$}(CN)$_3$]$^-$ group acting as a monodentate end-cap ligand. Magnetic data of **2** show the occurrence of intrachain ferromagnetic coupling (J = +11.4 cm^{-1} across bridging cyanide) and weak interchain antiferromagnetic interactions (J' *ca.* −0.07 cm^{-1}). These last ones are responsible for the observed metamagnetic behaviour of **2**, the value of the critical field being H_c = 700 G. The incipient frequency-dependence of the out-of-phase signal of **2** under applied dc field $H > H_c$ that is observed at $T < 4.5$ K supports the occurrence a slow relaxation of the magnetization, a feature which is reminiscent of the behaviour of the single chain magnets (SCMs). The use of the heteroleptic species [Fe{HB(pz)$_3$}(CN)$_3$]$^-$ as a ligand toward fully solvated metal ions and coordinatively unsaturated preformed complexes to prepare heterometallic complexes with new spin topologies is analyzed and discussed in the light of the available magneto-structural data.

1. Introduction

The discovery of slow reversal of the magnetization and quantum effects in discrete polynuclear complexes and chains has greatly renewed the interest in low-dimensional molecule-based magnetic compounds [1]. A common strategy to obtain such systems lies on the self-assembly of specially tailored building blocks containing the topological and electronic requirements, which are needed to obtain materials with the prefixed architecture and the desired properties [2].

The cyanide seems to be a suitable ligand in this perspective for two main reasons: (i) its ambidentate character facilitates the synthesis of heterometallic compounds; (ii) it has a remarkable ability to mediate ferro- or antiferromagnetic interaction between different metals and the prediction of the nature of the magnetic interaction on the basis of simple symmetry considerations is quite easy. Many of the cyanide-based molecular materials have been prepared by using quite stable hexacyanometallate complexes of formula [M(CN)$_6$]$^{(6-m)-}$ as ligands [3]. The well known three-dimensional Prussian Blue analogues are prepared by the reaction of these precursors with fully solvated metal ions and their properties closely depend on the nature of the metal ions and counterions. The synthesis of molecule-based magnets with a tunable Curie temperature [4] and photo- [5] or electro-chemically [6] induced magnetism are among the most spectacular results. Having in mind the extension of this chemistry toward lower dimensionality compounds with new spin topologies, the above fully solvated metal ion was replaced by the preformed complex [M′L$_x$S$_y$]$^{z-}$ [L and S being the blocking ligand and solvent, respectively] [7]. This strategy has afforded a rich family of compounds whose architecture and properties can be controlled to some extent by an adequate choice of the synthetic conditions, metal ions and blocking ligands. In particular researchers have been able to obtain

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high-nuclearity metal-cyanide compounds exhibiting high-spin ground states [8].

In the context of the exhaustive research efforts devoted to the magneto-structural studies on cyanide-containing metal complexes, we and other groups have developed an alternative synthetic route where the mononuclear complex $[M^{III}(L)(CN)_x]^{(x+l-3)-}$ (M = Fe, Cr or Ru; L = polydentate blocking ligand, l = charge of L) is the starting cyanide-bearing unit [9,10]. The use of a bidentate ligand L as the blocking group and the subsequent complex formation between the resulting tetracyano-bearing unit with either fully solvated metal ions or coordinatively unsaturated complexes has provided a great variety of discrete heterometallic species [11] as well as single- and double 4,2-ribbon like bimetallic chains [11c,12]. Some of these chains exhibit slow magnetic relaxation and hysteresis effects and they are known as single chain magnets (SCMs) [12b–d,12f,g]. The follow-up of our strategy has concerned the search for a new topology of the cyanide anionic building block which is represented by the complexes *mer*-$[Fe(bpca)(CN)_3]^-$ and *fac*-$[Fe\{HB(pz)_3\}(CN)_3]^-$ [$bpca^-$ = bis(2-pyridylcarbonyl)amidate and $HB(pz)_3^-$ = hydrotris(1 − pyrazolyl)borate] [13,14]. The T-shape of the three cyanide ligands in the former precursor is specially suited for the design of ladder-like systems [13] whereas the *fac* arrangement of the three cyanide groups in the latter one seems to determine the *fac* distribution of the three peripheral monodentate *fac*-$[Fe\{HB(pz)_3\}(CN)_3]^-$ ligands in the tetranuclear compound *fac*-{$[Fe^{III}\{HB(pz)_3\}(CN)_2(\mu\text{-}CN)]_3Fe^{III}(H_2O)_3$} [14]. It deserves to be noted that recently, other groups have used this last precursor to prepare low-dimensional heterometallic species [15–17], the most exciting ones among them being examples of Single Molecule Magnets (SMMs) [15c,16] and SCMs [17].

In this paper, we report the synthesis and characterization of the low-spin iron(III) precursor $[Li(H_2O)_4]$-*fac*-$[Fe\{HB(pz)_3\}(CN)_3]$ (**1**) and that of the neutral bimetallic chain $\{[Fe^{III}\{HB(pz)_3\}(CN)_3]_2[Ni^{II}(dpt)]\}_n \cdot 3nH_2O$ (**2**) (dpt = dipropylenetriamine) together with a thorough variable-temperature magnetic study of **2**.

2. Experimental

2.1. Materials and physical techniques

Nickel(II) perchlorate hexahydrate, anhydrous lithium perchlorate and dipropylenetriamine (dpt) were purchased from commercial sources and used as received. The mononuclear PPh_4-*fac*-$[Fe\{HB(pz)_3\}(CN)_3] \cdot H_2O$ precursor has been prepared by a previously reported procedure [14]. Elemental analyses (C, H, N) of **1** and **2** were performed by the Servicio de Microanálisis of the Universidad Autónoma de Madrid. The Fe/Ni ratio (2:1) of **2** was determined by SEM at the Servicio Interdepartamental of the Universitat de València. The IR spectra were recorded on KBr pellets of **1** and **2** with a Biorad FTIR spectrophotometer in the 400–4000 cm^{-1} region. Magnetic susceptibility measurements on polycrystalline samples of **1** and **2** were carried out with a Superconducting Quantum Interference Design (SQUID) magnetometer at room temperature (**1**) and in the temperature range 1.9–300 K (**2**) and under an applied field ranging from 50 G to 1 T. The magnetization measurements for **2** were done at 2.0 K in the range 0–5 T. The ac measurements on a polycrystalline sample of **2** were performed at frequencies ranging from 1 to 1000 Hz with an ac field amplitude of 1 G and under a dc field covering the range 0–800 G. The magnetic susceptibility data of **2** were corrected for the diamagnetic contribution of the constituent atoms through the Pascal constants (-466×10^{-6} cm^3 mol^{-1} per $Fe_2^{III}Ni^{II}$ unit) [18] and also for the sample holder.

Caution: Perchlorate salts are potentially explosive. Although no problems were experienced with the compound used, they should only be handled in small quantities, never scraped from sintered glass frits, nor heated in the solid state. Waste solutions containing cyanide were treated with basic solutions containing hypochlorite in order to transform cyanide into cyanate.

2.2. Preparation of $[Li(H_2O)_4]$-*fac*-$[Fe\{HB(pz)_3\}(CN)_3]$ (**1**)

Compound **1** was obtained as a yellow polycrystalline solid by a metathesis reaction of stoichiometric amounts of PPh_4-*fac*-$[Fe\{HB(pz)_3\}(CN)_3] \cdot H_2O$ and $LiClO_4$ in acetonitrile. The yield is practically quantitative. Red prisms of **1** which poorly diffract were obtained by recrystallization in water. μ_{eff} at room temperature is ca. 2.45 μ_B. *Anal.* Calc. for $C_{12}H_{18}FeN_9BO_4Li$ (**1**): C, 33.81; H, 4.23; N, 29.60. Found: C, 33.55; H, 4.11; N, 29.36 %.

2.3. Preparation of $\{[Fe^{III}\{HB(pz)_3\}(CN)_3]_2[Ni^{II}(dpt)]\}_n \cdot 3nH_2O$ (**2**)

PPh_4-*fac*-$[Fe\{HB(pz)_3\}(CN)_3] \cdot H_2O$ (0.2 mmol) dissolved in a methanol–water mixture (15 cm^3, 1:1 v/v) was added to an aqueous solution (10 cm^3) of $[Ni(dpt)(H_2O)_3](ClO_4)_2$ (0.1 mmol) [generated *in situ* by the reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ and dpt in a 1:1 molar ratio]. A white precipitate of PPh_4ClO_4 separates immediately. It was filtered off and the yellow mother liquor was allowed to stand at room temperature in a hood. **2** was obtained in a good yield (*ca.* 80%) as quadratic red prisms by slow evaporation of this solution in a few days. The preparation of X-ray quality crystals of **2** required the use of the water soluble precursor **1** as the cyanide source. Single crystal of **2** were obtained in H-shaped tube by slow diffusion of aqueous solutions containing **1** (0.05 mmol) in one arm and $[Ni(dpt)(H_2O)_3](ClO_4)_2$ (0.05 mmol) at the other one. The use of the lithium salt of the precursor to grow single crystals of **2** in water is preferred in order to avoid the contamination of **2** by the precipitation of the PPh_4ClO_4 salt. *Anal.* Calc. for $C_{30}H_{43}Fe_2NiN_{21}B_2O_3$ (**2**): C, 38.16; H, 4.55; N, 31.16. Found: C, 38.05; H, 4.31; N, 30.01%. The Ni/Fe metal ratio (1/2) was checked by SEM microanalysis.

2.4. Crystallographic data collection and structural determination

Crystallographic data of **2** were recorded at 250 K on a Kappa-CCD Bruker diffractometer with graphite mono-chromated MoKα

Table 1
Summary of the crystal data and structure refinement for $\{[Fe^{III}\{HB(pz)_3\}(CN)_3]_2[Ni^{II}(dpt)]\}_n \cdot 3nH_2O$ (**2**)

Formula	$C_{30}H_{36}B_2Fe_2N_{21}NiO_2$
F_w	914.78
Crystal system	monoclinic
a (Å)	15.7714 (18)
b (Å)	10.5732 (8)
c (Å)	25.698 (3)
α (°)	90
β (°)	92.001 (8)
γ (°)	90
V (Å^3)	4286.6 (8)
Z	2
Space group	$P2_1/n$
Linear absorption coefficient μ (cm^{-1})	11.59
Density ρ (g cm^{-3})	1.42
Merging R	0.0412
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0363
[a] $Rw = [\Sigma w(\|\|F_o\| - \|F_c\|\|)^2/\Sigma wF_o^2]^{1/2}$	0.0425
Goodness-of-fit	1.000
$\Delta\rho_{min}$ (e Å^{-3})	−0.37
$\Delta\rho_{max}$ (e Å^{-3})	0.57

[a] Weighting scheme defined as $w = w'[1 - ((\|F_o\| - \|F_c\|)/6\sigma(F_o))^2]^2$ with $w' = 1/\Sigma_r A_r T_r(X)$ and coefficients 1.64, 0.282, 1.27 and 0.0526 for a Chebyshev series for which $X = F_c/F_c(max)$.