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A versatile ethanolamine-derived trifluoromethyl enaminone ligand for the elaboration of nickel(II) and copper(II)–dysprosium(III) multinuclear complexes with magnetic properties

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ABSTRACT

A Ni(II) tetranuclear cubane-like complex and a mixed Cu(II)–Dy(III) nonanuclear complex have been synthesized from a common ethanolamine-derived trifluoromethyl enaminone ligand. The resulting polynuclear architectures exhibit interesting magnetic properties arising from the metallic architecture, especially Single-Molecule Magnet (SMM) behavior. The crystal structures of the [Ni_4] and [Dy_3Cu_6] complexes were refined by single-crystal X-ray diffraction analyses and correlated to variable-temperature magnetic susceptibility data. Redox properties of the Ni(II) tetranuclear complex have been also investigated. The [Dy_3Cu_6] complex results from the condensation of three {Dy_2Cu_2} cubane-like moieties giving rise to nonanuclear architectures. By changing the global charge of the Cu–Dy nonanuclear complex (from cationic to neutral), compared with those previously reported in the literature, the magnetic properties have been disturbed. This work should contribute to improve the SMM synthesis strategy.

1. Introduction

β-Aminovinyl ketones with a fluoroalkyl moiety are attractive organic entities for the design of original materials as they can coordinate numerous metal ions *via* coordination chemistry routes [1] and can be also considered as versatile building blocks that can be decorated in a number of synthetic sequences, to produce diverse scaffolds specifically designed for applications [2]. Moreover, these enaminones offer great potential for generating molecular diversity (see the general structure in Fig. 1) because these organic substrates can be structurally modified at different sites (R_1, R_2, R_3 and R_4) by variation of (i) the amine (R_1), (ii) the substitution on the C=C double bond (R_2 and R_3) and (iii) the fluoroalkyl moiety (R_4) [2d–e]. Therefore organic functionalities with specific properties can be in principle attached at the four positions of the enaminone using readily available starting materials and different synthetic strategies.

In previous studies, we used a Cu(II) cubane complex [$Cu_4(\mathbf{L})_4$], built from an ethanolamine-derived enaminone ligand ($R_1 = C_2H_4OH$, $R_2 = CH_3$, $R_3 = H$ and $R_4 = F$), to elaborate heterometallic structures and, in particular, a nonanuclear [Cu_6Ln_3] Single-Molecule Magnet (SMM) [3]. We also recently synthesized additional ethanolamine-derived enaminone ligands ($R_1 = C_2H_4OH$, $R_3 = H$ and $R_4 = F$) with organic entitites such as R_2 = bodipy, azobenzene and anthracene, exhibiting interesting optical properties in order to design copper(II) cubane architectures with potential specific properties [4,5].

In this work, we focused our attention on the use of one of these ligands ($\mathbf{L^1H_2}$, see Fig. 1b, $R_1 = C_2H_4OH$, R_2 = phenyl, $R_3 = H$ and $R_4 = F$) [4] with the aim (i) to extend our studies towards the synthesis of a Ni(II) complex (**1**) and also mixed Cu(II)–Dy(III)

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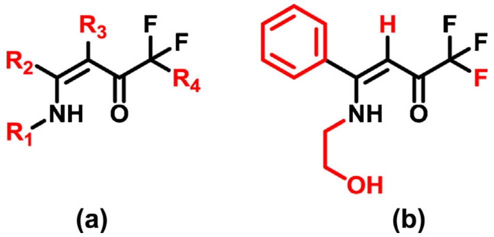

Fig. 1. (a) Fluoroalkylated enaminone: a versatile building block for the design of task-specific ligands (R_1 = aryl, heterocycle, alkyl; R_2 = H, aryl, heterocycle, alkyl; R_3 = H, Br, Cl, I, alkyne, aryl, heterocycle, alkyl, R_4 = Br, Cl, F, H, CHOHAr with Ar = aryl, heterocycle); (b) $\mathbf{L^1H_2}$ ethanolamine-derived ligand used in this study to prepare complexes **1** and **2**.

Single-Molecule Magnet complex (**2**); (ii) to compare their structure, properties with our previous Cu(II) cubanes and SMMs [3,4]. This model ligand could be considered as an entry to the elaboration of multifunctional single-molecule magnets (SMMs) combining properties of the metal ions core and ligand entity, as the phenyl group (R_2) can be easily replaced by other organic more elaborated functions (radical, optic, redox, etc.). On the other hand, the presence of possible F···F and F···H interactions due to the presence of trifluoromethyl group may possibly organize the intermolecular complexes architectures. The fact that some metal coordination clusters can exhibit single-molecule magnets (SMMs) behavior [6] is still an area of intensive research in relation to potential applications in magnetic information processing and storage [7]. Indeed, SMMs are molecules that can be magnetized in a magnetic field and retain the magnetization when it is switched off during a certain time. One of the main goals of current research is to elaborate metal ions-based complexes which could exhibit long relaxation times as this special point is crucial for information storage applications [8]. In that context, the use of lanthanide ions, such as Dy(III) has many advantages. Their large spins and pronounced spin-orbit coupling result in strong Ising-Type magnetic anisotropy [9] leading, even in case of mononuclear complexes (Single-Ion Magnet, SIM), to SMMs properties [10]. Moreover, the association of 3d and 4f transition-metal ions within a single complex help to increase the ground spin state through d–f magnetic interactions [11]. Lanthanides ions, with their high coordination numbers and geometries, are in that case useful for engineering large polynuclear clusters. Accordingly, most efforts devoted to the chemical design of SMMs concentrate on the synthesis of large clusters with both high spin and anisotropy. In this regard metal complexes with cubane-like structures are interesting starting points to elaborate high-spin molecules as generally ferromagnetic exchange couplings and high-spin ground state can be anticipated. Therefore, cubane-like compounds have received a considerable attention for many decades [12]. Illustrative of this, several lanthanide-containing complexes exhibiting SMM behavior have been recently reported [13]. Whereas some of them are based on the only lanthanide ion, the combination of 4f and 3d transition metal ions has turned out to be most successful.

Nevertheless, the role of the organic moiety of these complexes is still primordial as the ligand will built the final coordination architecture generating favorable magnetic interactions between metal ions in order to observe SMM behavior. The ligand can also bring intrinsic properties (magnetic, optic, redox, etc.) which can interact, possibly in a cooperative mode, with the magnetic properties of the metal ions within the complex. Last but not least, additional interest of cubanes bearing redox active metallic centers, are their potential use in catalysis [14].

2. Results and discussion

2.1. Complexes syntheses

The two complexes **1** and **2** were obtained from the deprotonated ligand ($\mathbf{L^1}$) with DBU as the base. Then, a methanolic solution of $NiCl_2.6H_2O$ was added to induce, after heating, the formation of the cubane complex **1**. According to the construction of the cluster **2**, the reaction was performed in sequence with first the addition of $Dy(NO_3)_3{\cdot}5H_2O$ to generate the formation of an intermediate dysprosium complex followed by the addition of $CuCl_2{\cdot}2H_2O$ to get the nonanuclear Cu(II)–Dy(III) complex **2**. It is interesting to note that the same reaction performed with $NiCl_2{\cdot}6H_2O$ instead of $CuCl_2{\cdot}2H_2O$ after the dysprosium addition, allowed us to get only the cubane **1**. This observation could be explained by the poorer reactivity of the Ni(II) ion compared to Cu(II).

2.2. Crystal structures of complexes

$\mathbf{[Ni_4(L^1)_4(MeOH)_4]}$ (**1**)[1]: the nickel-based complex **1** adopts a tetrahedral type structure and can be described as four metal ions located on half of the tops of a cube (Fig. 2a). The four other tops of this cubane-like architecture are occupied by oxygen atoms belonging to the four deprotonaed alcohol arm of the four $\mathbf{L^1}$ ligands. The coordination spheres of the Ni(II) ions are completed by one oxygen atom (ketone entity of the enaminone), one nitrogen atom from one $\mathbf{L^1}$ ligand and one last oxygen atom from one coordinated protonated μ-OCH_3 solvent molecule. The resulting $[Ni_4(\mathbf{L^1})_4(MeOH)_4]$ complex is then neutral with a slightly distorted $\{Ni_4O_4\}$ core, as the Ni–O–Ni angles range from 94.3(1)° to 100.8(1)° (theoretical value: 90°) as well as the O–Ni–O angles which vary from 80.5(1)° to 106.5(1)° (theoretical value: 90°) and from 162.2(1)° to 174.4(1)° (theoretical value: 180°). The Ni–O bond lengths within the cubane core are regular as they vary less than 0.02 Å around the mean value. The coordination polyhedron of each Ni(II) is almost a regular octahedron, as the O–Ni–O angles only deviate from 90° by less than 7° and the Ni–O bond lengths vary by less than 0.12 Å around the mean value of 2.064 Å. However, once can note that the Ni–$OHCH_3$ (2.163 Å) and the Ni–N (2.001 Å, belonging to the $\mathbf{L^1}$ ligand) bond lengths are slightly longer and shorter, respectively, than the other Ni–O ones. Of the six Ni···Ni distances, four are around 3.049 Å while the two other are around 3.167 Å. This $\{Ni_4O_4\}$ cubane core can be called as [2 + 4] following Ruiz and co-workers classification [15]. [Ni4] complexes are well isolated one from each other's as the shortest distance (centroid to centroid) between two neighboring [Ni4] complexes is equal to 8.9 Å.

The structural cohesion is maintained by the presence of numerous inter-complexes F···H interactions in order to build a rigid 3-D network.

$\mathbf{[Dy_3Cu_6(L^1)_6(\mu_3\text{-}OH)_6(H_2O)_6(OH)_6]}$ (**2**)[2]: The structure of this nonanuclear mixed Cu(II)–Dy(III) is similar with the one previously reported except on the charge supported by the complex (neutral complex in our case *vs* cationic complex) [3]. The complex is built

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[1] Complex **1**: CCDC 1061692, triclinic, P-1, a = 12.803(1) Å, b = 13.694(1) Å, c = 17.754(2) Å, α = 94.237(7)°, β = 107.302(8)°, γ = 98.199(8)°, V = 2919.0(4) Å^3, refined formula: $C_{52}H_{56}F_{12}N_4Ni_4O_{12}$, molecular weight = 1391.9 g mol^{-1}, Z = 2, d = 1.593, μ = 1.379 mm^{-1}, $R(I/\sigma(I) > 3)$ = 0.0665, $R_w(I/\sigma(I) > 3)$ = 0.0806, S = 1.12, $\Delta\rho_{max}$ = 2.10 e$^-$ Å^{-3}, $\Delta\rho_{min}$ = −2.10 e$^-$ Å^{-3}, no. refined parameters: 757, No. reflections used: 8573.

[2] Complex **2**: CCDC 1061691, cubic, I-43d, $a = b = c$ = 35.431(5) Å, $\alpha = \beta = \gamma$ = 90°, V = 44479(11) Å^3, refined formula: $C_{72}H_{78}Cu_6Dy_3F_{18}N_6O_{24}$, molecular weight = 2622.2 g mol^{-1}, Z = 16, d = 1.585, μ = 3.203 mm^{-1}, $R(I/\sigma(I) > 3)$ = 0.0761, $R_w(I/\sigma(I) > 3)$ = 0.0884, S = 1.08, $\Delta\rho_{max}$ = 2.63 e$^-$ Å^{-3}, $\Delta\rho_{min}$ = −1.97 e$^-$ Å^{-3}, no. refined parameters: 395, No. reflections used: 5225.