Área: INO

Trinuclear nickel(II) and cobalt(II) triple helicates with a multidentate bithiazole(bis)oxamato ligand as supramolecular nanomagnets

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Keywords: *Oxamate, Magnetic Properties, Metallosupramolecular Complexes.*

Highlights

Nickel(II) and cobalt(II)-mediated self-assembly of the tris(chelating) *N,N'*-2,2'-(4,4'-bithiazole)bis(oxamate) ligand leads to a new metal-organic supramolecular nanomagnets featuring a unique linear triple-stranded trinuclear structure of the helicate-type.

Abstract

The supramolecular coordination chemistry offers convenient tools for the current evolution from molecular magnetism toward molecular spintronics and quantum computation.[1] Our group have been recently working with the *N,N'*-2,2'-(4,4'-bithiazole)bis(oxamate)[2] ligand (L) and herein we report the synthesis and general physical characterization, molecular and crystal structures, as well as the study of the static and dynamic magnetic properties of the compounds of formula $Na_6Ni_3L_3 \cdot 11H_2O \cdot MeOH$ (**1**) and $K_6Co_3L_3 \cdot 8H_2O \cdot MeOH$ (**2**). **1** and **2** were obtained by the stoichiometric reaction (1:1 molar ratio) of the diethyl ester derivative of the ligand (H_2Et_2L) and either nickel(II) or cobalt(II) nitrate salt in basic aqueous media. The IR spectra of **1** and **2** show the occurrence of two strong intensity peaks at 1615 and 1590 (**1**) or 1616 and 1595 cm^{-1} (**2**) [ν(C=O)] show a significantly displacement when compared to the IR spectrum of the proligand suggesting a coordination of the oxamate groups. Furthermore, the shift of the thiazole skeleton bands from 1476, 1439 and 1302 cm^{-1} in the IR spectrum of H_2Et_2L to 1523, 1454 and 1325 (**1**) or 1521, 1450 and 1321 cm^{-1} (**2**) is also indicative of the coordination by the thiazole groups. X-ray powder diffraction performed on crushed crystals of **1** and **2** suggests they are isostructural compounds and reproduce well the diffraction patterns calculated based on the crystal structures. **1** crystallize in the C2/c and **2** crystallize int the $P2_1/n$ both in the monoclinic space group. The asymmetric unit of both contains a triple-stranded trinuclear complex anion of helicate-type, $[M^{II}_3L_3]^{6-}$, formed by three L^{4-} ligands wrapping around three Ni^{II} (**1**) or Co^{II} ions (**2**) in a linear array. Six crystallographically independent Na^{I} (**1**) and K^{I} ions (**2**) complete the asymmetric unit, together with water and methanol coordinated molecules that results in a crystal packing of an oxamato-bridged heterometallic $A^{I}M^{II}$ 3D structure with an intricate pillared double mixed triangular/rhombic layered architecture. The *dc* magnetic measurements reveal a very weak antiferromagnetic coupling between the Ni^{II} ions for **1** which contrasts with the moderate antiferromagnetic coupling between the Co^{II} ions through the amidothiazole bridges for **2** [$-J$ = 0.31 (**1**)/1.80 cm^{-1} (**2**); $\mathbf{H} = -J\,(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3)$ with $S_1 = S_2 = S_3 = 1$]. The *ac* magnetic measurements show a slow magnetic relaxation (SMR) at relatively low applied *dc* magnetic fields for **2**, whereas no SMR effects are observed for **1** regardless of the magnitude of the applied *dc* magnetic field. A simple analysis of the *ac* magnetic data through the Arrhenius model reveals a thermal-assisted Orbach mechanism for the spin relaxation dynamics of **2** with values of the energy activation and pre-exponential factor typical of field-induced cobalt(II)-based single-molecule magnets [E_a = 6.1 and 6.4 cm^{-1} with $\tau_0 = 4.0$ and 5.4×10^{-8} s at H_{dc} = 2.5 and 5.0 kOe, respectively]. These compounds are candidates to obtain a new class of magnetic metal-organic frameworks.

[1] Ferrando-Soria et al. *Coord. Chem. Rev*. **2017**, 339, 17-103.
[2] Kalinke et al. *Cryst. Growth Des*. **2019**, 19, 3905-3912.

Acknowledgments

CAPES, CNPq, IFG, UFG.