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New coordination polymers based on a novel polynitrile ligand: Synthesis, structure and magnetic properties of the series $[M(tcnoetOH)_2(4,4'\text{-bpy})(H_2O)_2]$ ($tcnoetOH^- = [(NC)_2CC(OCH_2CH_2OH)C(CN)_2]^-$; M = Fe, Co and Ni)

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Dedicated to Dante Gatteschi ("il capo di tutti capi") not only for his scientific work but especially for his sparkling wit and *magnetic* personality.

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ABSTRACT

A novel polynitrile anionic ligand, $tcnoetOH^-$ (=$[(NC)_2CC(OCH_2CH_2OH)C(CN)_2]^-$), has been synthesized by a one-pot reaction from a cyclic acetal and malononitrile. This ligand has been successfully used to prepare, with 4,4′-bpy as co-ligand, a novel series of coordination polymers formulated as $[M(tcnoetOH)_2(4,4'\text{-bpy})(H_2O)_2]$ with M(II) = Fe (**1**), Co (**2**) and Ni (**3**). These isostructural compounds present a linear chain structure consisting of octahedrally coordinated metal ions bridged by trans 4,4′-bpy ligands. The coordination sphere of the metal ions is completed with two terminal $tcnoetOH^-$ ligand and two water molecules. The magnetic properties indicate that the three compounds are paramagnetic, as expected from the long 4,4′-bpy bridge connecting the metal atoms. Their magnetic properties have been fitted with a model of isolated ions including a zero field splitting for the Fe(II) and Ni(II) derivatives.

1. Introduction

In recent years, a huge effort has been devoted to the synthesis of novel potentially polydentate ligands in order to create high dimensional coordination structures with magnetic [1] and catalytic properties [2]. Among these polydentate ligands, the carboxylates and polynitriles ones are two of the most used ligands since they can act in a vast number of coordination modes [3] from mono- to multidentate in order to generate high dimensional magnetic polymers mainly with first-row transition metals [4]. Besides these ligands, aromatic N-containing ligands such as pyridine, 2,2′- and 4,4′-bipyridine, bipyrimidine, terpyridine, and phenanthroline, have also been extensively used to create 1D, 2D and 3D structures with different magnetic ions [5].

Anionic polynitrile ligands are very interesting due to their ability to act as bridging ligands with different coordination modes to generate many different topologies by themselves [6] and when used with other co-ligands [7]. Among the advantages of the polynitrile ligands, their rigidity and electronic delocalization make them very suitable ligands for the synthesis of high dimensional coordination polymers with different magnetic anions. Furthermore, the ease of their synthesis and the possibility of substituting one or more cyano groups by other potentially coordinating groups as –OH, –SH or $–NH_2$ provide an increased interest of these ligands. The rich coordination chemistry of the polynitrile ligands has been clearly demonstrated for different anionic polynitrile ligands as $tcnoet^-$ ($[(NC)_2CC(OEt)C(CN)_2]^-$, Scheme 1) that has led to the synthesis of several series of extended coordination polymers when used alone [8] or in combination with different co-ligands [7i,9].

In order to improve the coordination abilities of this anionic ligand, we have explored the possibility to include extra potentially coordinating groups in order to stabilize other high dimensional topologies. Thus, we have added an additional –OH group to the $tcnoet^-$ ligand to obtain a novel polynitrile anionic ligand: $tcnoetOH^-$(=$[(NC)_2CC(OCH_2CH_2OH)C(CN)_2]^-$, Scheme 1) that presents up to five terminal potentially coordinating groups (one –OH group and four –CN groups). Here, we present the synthesis of this novel ligand and the synthesis, structural and magnetic characterization of the series of coordination polymers of formula $[M(tcnoetOH)_2(4,4'\text{-bpy})(H_2O)_2]$ with M(II) = Fe (**1**), Co (**2**) and Ni

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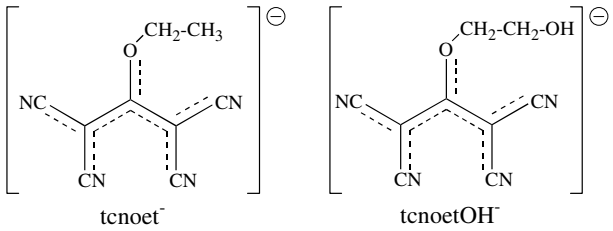


Scheme 1.

(**3**), obtained using this polynitrile ligand with 4,4-bipyridine as the co-ligand.

2. Experimental

2.1. Materials

4,4′-Bipyridine 98%, tetracyanoethylene, potassium *t*-butoxide, iron(II) chloride tetrahydrate, cobalt(II) chloride hexahydrate and nickel(II) chloride hexahydrate were used as received. The 2-(1,3-dioxolan-2-ylidene)malononitrile (Scheme 2) was prepared by reaction in ethylene glycol of tetracyanoethylene with urea as previously described in Ref. [10].

2.2. Syntheses

2.2.1. K[tcnoetOH]

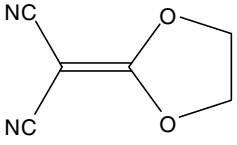
$K[(NC)_2CC(OCH_2CH_2OH)C(CN)_2]$ was prepared following a similar procedure as described in Ref. [8] for the related tcnoet$^-$ ligand (Scheme 1). A warm ethanolic solution (15 mL) of malononitrile ($CH_2(CN)_2$) (400 mg, 6 mmol) and potassium *t*-butoxide (C_4H_9OK) (676 mg, 6 mmol) was added to a warm ethanolic solution (20 mL) of 2-(1,3-dioxolan-2-ylidene)malononitrile (Scheme 2) (816 mg, 6 mmol). The mixture was refluxed for 2 h. On cooling, a beige powder precipitate appeared which was filtered on a sintered-glass fritted and air-dried (yield: 902 mg, 63%). NMR spectra (acetone-d_6) ^{1}H: 4.26: CH_2 (2H, t, $J = 7$ Hz), 3.78: CH_2 (2H, td, $J = J' = 7$ Hz), 3.71: OH (1H, d, $J = 7$ Hz). ^{13}C NMR 182.78 (C–O), 117.54 (CN), 76.93 (CH_2), 61.59 (CH_2), 46.58 $C(CN)_2$. IR data (ν, cm^{-1}): 3547s, 3460br, 2202s, 1638w, 1507s, 1419m, 1352m, 1168m, 1072m, 993m.

2.2.2. [Fe(tcnoetOH)$_2$(4,4′-bpy)(H$_2$O)$_2$] (**1**)

Under aerobic conditions, an ethanolic solution (15.6 mL) of 4,4′-bipyridine (78 mg, 0.5 mmol) was added with stirring at room temperature to an aqueous solution (2 mL) of $FeCl_2 \cdot 4H_2O$ (99 mg, 0.5 mmol). An aqueous solution (9 mL) of K[tcnoetOH] (241 mg, 1 mmol) was added to the resulting solution. A rust-coloured precipitate that quickly appeared in the final yellow solution was filtered. Slow evaporation of the filtrate at room temperature afforded golden single crystals suitable for X-ray structure determination. IR data (ν, cm^{-1}): 3431m, 3300br, 2234m, 2201s, 1610w, 1508w, 1498s, 1460m, 1398m, 1148m, 1068m.

2.2.3. [Co(tcnoetOH)$_2$(4,4′-bpy)(H$_2$O)$_2$] (**2**)

This compound was prepared by the procedure of **1** but using $CoCl_2 \cdot 6H_2O$ (118.5 mg, 0.5 mmol) instead of $FeCl_2 \cdot 4H_2O$. In this case a mauve precipitate appeared from the solution. Slow evaporation of the filtrate at room temperature afforded orange single crystals suitable for X-ray structure determination. IR data (ν, cm^{-1}): 3436 m, 3337br, 2238m, 2201s, 1736s, 1720s, 1611w, 1497s, 1460m, 1398m, 1377m, 1150m, 1068m.



Scheme 2.

2.2.4. [Ni(tcnoetOH)$_2$(4,4′-bpy)(H$_2$O)$_2$] (**3**)

This compound was prepared by the procedure of **1** but using $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol) instead of $FeCl_2 \cdot 4H_2O$. In this case, a grey precipitate appeared from the solution. Slow evaporation of the filtrate at room temperature afforded green single crystals suitable for X-ray structure determination. IR data (ν, cm^{-1}): 3440m, 3311br, 2244m, 2199s, 1736s, 1720s, 1609w, 1497s, 1460m, 1398m, 1346m, 1150m, 1068m.

2.3. Physical measurements

Infrared spectra were recorded in the range 4000–400 cm^{-1} as KBr pellets on a FT-IR NICOLET 5700FT-IR Spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX 3-400 spectrometer. Chemical shifts are reported in δ units (parts per million) downfield from TMS (^{1}H) or from the solvent resonance as an external reference (^{13}C).

Variable temperature susceptibility measurements were carried out in the temperature range 2–300 K with a d.c. applied magnetic field of 0.1 T on polycrystalline samples of the three compounds with a Quantum Design MPMS-XL-5 SQUID magnetometer. The isothermal magnetizations were made at 2 K with magnetic fields of up to 5 T. The susceptibility data were corrected for the sample holder previously measured using the same conditions and for the diamagnetic contributions of the salt as deduced by using Pascal's constant tables ($\chi_{dia} = -403.2 \times 10^{-6}$, -402.2×10^{-6} and -402.2×10^{-6} emu mol^{-1} for **1**–**3**, respectively).

2.4. X-ray crystallography

Data for compounds **1**–**3** were collected, at 170 K, with a Xcalibur 2 Diffractometer (Oxford Diffraction) using a graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and successive Fourier difference syntheses, and were refined on F^2 by weighted anisotropic full-matrix least-squares methods [11]. All non-hydrogen atoms were refined anisotropically, except the two C8 and C9 carbon atoms of compound **3**, which were refined isotropically. For compounds **1**–**2**, all the hydrogen atoms were located by difference Fourier map, and then refined isotropically. For compound **3**, the hydrogen atoms are not located by difference Fourier map; the atoms attached to the 4,4′-bpy are calculated while those attached to the water molecule and to the terminal oxygen of the polynitrile ligand ($-O(CH_2)_2-OH$) are not calculated. Scattering factors and corrections for anomalous dispersion were taken from the *International Tables for X-ray Crystallography* [12]. The thermal ellipsoid drawings were made with the ORTEP program [13]. Data collection and data reduction were done with the CRYSALIS-CCD and CRYSALIS-RED programs [14]. All other calculations were performed with standard procedures (WINGX) [15]. Pertinent crystal data and structure refinement, and selected bond distances and angles are listed in Tables 1–3, respectively.

3. Results and discussion

3.1. Synthesis and IR spectroscopy

The synthesis of the novel polynitrile anionic ligand tcnoetOH$^-$ has been easily performed following the method used to prepare