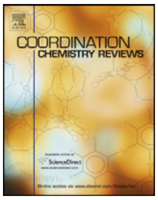
Coordination Chemistry Reviews 254 (2010) 1468–1478

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Polynitrile anions as ligands: From magnetic polymeric architectures to spin crossover materials

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Contents

ARTICLE INFO

Article history:
Received 26 August 2009
Accepted 12 November 2009
Available online 5 December 2009

Keywords:
Polynitrile
Magnetic properties
Cyano ligand
Nitrile ligand
Coordination polymers
Metal(II) complexes
Magnetic transition
Structural transition
Thermochromism

ABSTRACT

The use of polynitrile anions as ligands (L) either alone or in combination with neutral co-ligands (L′) is a very promising and appealing strategy to get molecular architectures with different topologies and dimensionalities thanks to their ability to coordinate and bridge metal ions in many different ways. The presence of several potentially coordinating nitrile groups (or even other donor groups as –OH, –SH or –NH$_2$), their rigidity and their electronic delocalization allow the synthesis of original magnetic high dimensional coordination polymers with transition metals ions. Furthermore, these ligands have shown coordinating and bridging capabilities in novel discrete and polymeric bistable materials (materials showing original magnetic behaviours or spin crossover (SCO) transitions). Here we report an overview of the results obtained with some of these modified polynitrile ligands, showing their rich coordination chemistry and their crucial role in new molecular materials exhibiting unusual magnetic transitions.

Abbreviations: dca$^-$, dicyanamide anion; tcm$^-$, tricyanomethanide anion; tcnq$^-$, 7,7′,8,8′-tetracyanoquinodimethane anion; dcnome$^-$, 2,2-dicyano-1-methoxyethenolate anion; dcnoet$^-$, 2,2-dicyano-1-ethoxyethenolate anion; dcnoetOH$^-$, 2,2-dicyano-1-(2-hydroxyethoxy)-ethenolate anion; tcno^{2-}, 1,1,3,3-tetracyano-2-oxopropenide dianion; tcnome$^-$, 1,1,3,3-tetracyano-2-methoxypropenide anion; tcnoet$^-$, 1,1,3,3-tetracyano-2-ethoxypropenide anion; tcnopr$^-$, 1,1,3,3-tetracyano-2-propoxypropenide anion; tcnoetOH$^-$, 1,1,3,3-tetracyano-2-(2-hydroxyethoxy)propenide anion; tcnopr3OH$^-$, 1,1,3,3-tetracyano-2-(3-hydroxypropoxy)-propenide anion; tcnopr2OH$^-$, 1,1,3,3-tetracyano-2-(2-hydroxypropoxy) propenide anion; tcpd^{2-}, 2-dicyanomethylene-1,1,3,3-tetracyanopropenediide dianion; 2,2′-bpy, 2,2′-bipyridine; 4,4′-bpy, 4,4′-bipyridine; 2,2′-bpym, 2,2′-bipyrimidine; en, ethylenediamine; tn, 1,3-diaminopropane; abpt, 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole.

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doi:10.1016/j.ccr.2009.11.011

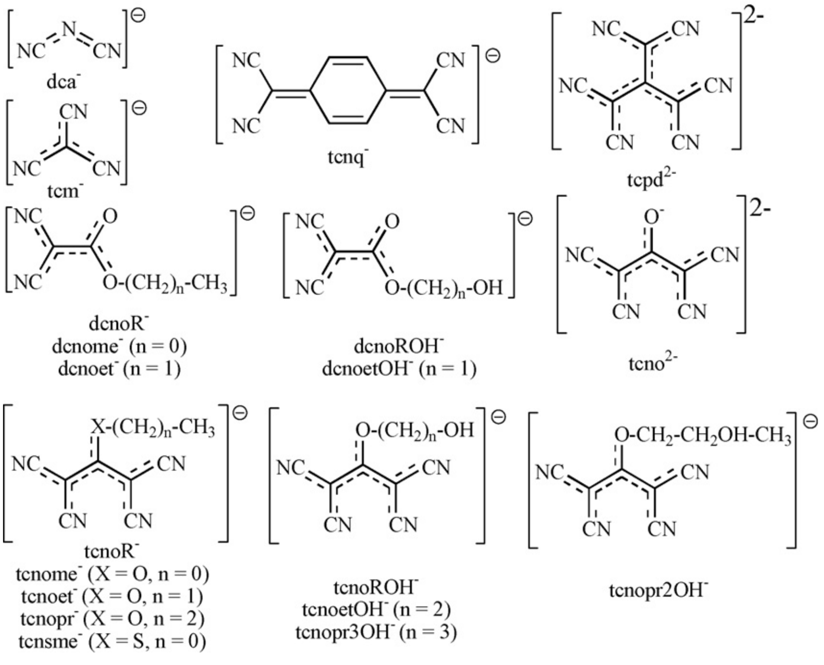
1. Introduction

The use of the coordinating capabilities of the cyano group (–CN) to bond different transition metals dates back three centuries ago, when M. Diesbach prepared a bright blue pigment by boiling blood [1]. This blue compound, known as Prussian blue (PB), can be formulated as $\mathrm{Fe^{III}}_4[\mathrm{Fe^{II}(CN)_6}]_3\cdot 14\mathrm{H_2O}$ and presents a cubic structure already proposed by Keggin and Miles [2] in 1936 and later modified by Ludi, Güdel et al. [3]. The magnetic and electronic properties of the original PB compound showed that this compound presents a long range magnetic ordering with $T_c = 5.6$ K [4] and that there exist a small, although non-negligible, spin density on the "a priori" diamagnetic $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ bridge connecting the paramagnetic Fe(III) centres [5]. Since these pioneering works, the vast family of PB derivatives has been enlarged and nowadays, this family presents many different derivatives that can be formulated as $\mathrm{A}_k\mathrm{M}_x[\mathrm{M'(CN)_6}]_y\cdot n\mathrm{H_2O}$, where A is a monovalent cation and M and M′ are divalent or trivalent transition metal ions [6]. From the magnetic point of view, the cyanide ligand is also unique since it presents predictable and easy to modulate magnetic couplings [7] that have led to the synthesis of metal cyanides exhibiting many different magnetic phenomena as high spin clusters [8], meta-magnetism [9], spin-glass behaviour [10], photo-magnetism [11], single molecule magnets (SMM) [12] and even magnetic ordering above room temperature [13].

Besides the cyano group itself (–CN), there exist a vast family of cyano-containing ligands [14], from the simple dicyanamide ($\mathrm{dca^-} = \mathrm{N(CN)_2}^-$) and tricyanomethanide ($\mathrm{tcm^-} = \mathrm{C(CN)_3}^-$) ligands to the more sophisticated polynitrile ligands as the dcnoet$^-$, dcnoetOH$^-$, tcnoR$^-$, tcnoROH$^-$ and tcpd^{2-} ligands (see Scheme 1). Concerning the dca$^-$ and tcm$^-$ ligands, Batten and Murray have recently published a very interesting revision (mainly focussed on extended structures) where they have clearly shown the ability of these simple polynitrile ligands to form 1D, 2D and 3D coordination polymers exhibiting interesting magnetic properties [15a]. Furthermore, these simple polynitrile ligands have also been combined with diamagnetic Cu(I) ions and organic donors of the TTF-type (TTF = tetrathiafulvalene) to prepare organic superconductors such as the $\mathrm{(BEDT{-}TTF)_2Cu(dca)X}$ series (BEDT–TTF = bis(ethylenedithio)tetrathiafulvalene; $\mathrm{X^-} = \mathrm{CN^-}$, $\mathrm{Cl^-}$ and $\mathrm{Br^-}$) [15b].

In the present account, we will focus on the work done with more sophisticated polynitrile ligands involving a variable number of cyano groups as those displayed in Scheme 1. These anions constitute a large family of very attractive ligands from both, the geometrical and the electronic points of view, which can be used to prepare extended architectures with interesting magnetic and electronic properties. The main characteristics that render these ligands very useful and suitable for this goal are: (i) their special geometries preclude the chelating coordination mode, forcing them to act as either terminal or (poly)bridging ligands; (ii) the electronic delocalization shown by these anions in their central skeletons may facilitate the existence of π–π overlap with other ligands and/or the transmission of electronic effects between the metal atoms and (iii) some polynitrile ligands can be reduced (or oxidized) to generate radical species that may increase the magnetic coupling with the metal ions coordinated to the polynitrile ligand. Although not very numerous, there are some examples of reduced polynitrile anions such as $\mathrm{tcnq}^{\bullet-}$ and $\mathrm{tcne}^{\bullet-}$ that have been combined with magnetic cations as Cu(II) and Ni(II) [16]. Other polynitrile ligand that has shown this possibility (although it has not been combined with magnetic ions yet), is the diamagnetic dianion $\mathrm{C_{10}N_8}^{2-}$ (=1,1,2,5,6,6-hexacyano-3,4-diazahexa-1,5-dienediide), which has been oxidized to the $(\mathrm{C_{10}N_8})^{\bullet-}$ radical anion [17]. An additional advantage of this family of ligands is the fact that most of them are easy to prepare and to modify with additional potentially coordinating groups such as oxo, thio, alkoxo, thiol or even amine groups, leading to polydentate ligands with different metal affinities and ligand fields.

The work presented here will be divided into two main groups: (i) M–L "binary compounds" prepared exclusively with polynitrile ligands (chapter 2) and (ii) M–L–L′ "ternary compounds" prepared with polynitrile ligands and neutral co-ligands acting either as terminal or bridging ligands (chapter 3).



Scheme 1. Polynitrile ligands's family portrait.

2. Polynitrile anions as ligands (L)

The use of polynitrile anions as ligands alone has produced a large variety of compounds and families with many different structures, from discrete molecules to 1D, 2D and 3D coordination polymers (Table 1). In this section we will present the main results obtained by using different polynitrile anions such as: dcnome$^-$ ([(CN)$_2$CC(O)OMe]$^-$), dcnoet$^-$ ([(CN)$_2$CC(O)OEt]$^-$) [18], dcnoetOH$^-$ ([(NC)$_2$CC(O)OEtOH]$^-$) [19], tcnoet$^-$ ([(NC)$_2$CC(OEt)C(CN)$_2$]$^-$), tcnopr3OH$^-$ ([(NC)$_2$CC(O–(CH$_2$)$_3$–OH)C(CN)$_2$]$^-$) [20], tcno^{2-} ([(NC)$_2$CC(O)C(CN)$_2$]$^{2-}$) [21] and tcpd^{2-} (C[C(CN)$_2$]$_3{}^{2-}$) with different transition metals ions as Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and even Zn(II) (see Table 1).

2.1. M:L binary systems (M = transition metal ion)

2.1.1. Dinitrile ligands

2.1.1.1. dcnoet$^-$ ([(CN)$_2$CC(O)OEt]$^-$) with Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II). This polynitrile ligand has been combined with Mn(II) (**3**), Fe(II) (**4**), Co(II) (**5**), Ni(II) (**6**), Cu(II) (**7**) and Zn(II) (**8**) [18]. All the metal ions, except Cu(II), give rise to an isostructural series formulated as [M(dcnoet)$_2$(H$_2$O)$_2$] where the metal ions present a MN$_4$O$_2$ environment formed by four N atoms from four different dcnoet$^-$ ligands and two *cis*-water molecules. The Cu(II) derivative has only one water molecule and can be formulated as [Cu(dcnoet)$_2$(H$_2$O)] (**7**) where the Cu(II) ion presents a CuN$_4$O environment formed by four N atoms from four different dcnoet$^-$ ligands and one water molecule. In all these compounds each polynitrile ligand bridges two metal atoms through the two different –CN groups, giving rise to a chain with double "NC–C–CN" bridges connecting the metal atoms (Fig. 1a). These double bridges generate 12-membered rings containing two metal atoms and two "NC–C–CN" bridges. Since the cyano groups coordinate *cis* positions of the metal atoms, leaving two *cis* positions free, the 12-membered dimetallacycles are not co-planar but almost orthogonal, giving rise to zigzag chains running along the [1 0 1] direction (Fig. 1a). The two free positions are occupied by two water molecules in the case of Mn, Fe, Co, Ni and Zn. In the Cu derivative, the metal ion presents a five-coordination mode with a distorted trigonal bipyramid geometry since there is only one water molecule to complete the coordination sphere of the Cu(II) ion (Fig. 1b). The presence of several inter-chain H-bonds gives rise to a H-bonded 3D structure. The magnetic properties show the presence of very weak antiferromagnetic couplings in all the cases that were easily reproduced with a regular chain model [18]. Besides the dcnoet$^-$ ligand, the closely related ligand dcnome$^-$ ([(CN)$_2$CC(O)OMe]$^-$) has also been used to prepare magnetic coordination polymers with Mn(II) (**1**) and Cu(II) (**2**) [22]. Interestingly, this slightly smaller ligand has also afforded chains with 12-membered dimetallacycles when combined with Mn(II) although with almost co-planar rings since the water molecules occupy *trans* positions, as observed in the Fe(II) derivative of the related dcnoetOH$^-$ ligand (see below and Fig. 2a). Furthermore, the Cu(II) derivative shows a different connectivity where each Cu(II) centre is linked to four different Cu(II) ions through "NC–C–CN" bridges, to generate a rectangular layer as the one displayed by the Co(II) derivative with the related dcnoetOH$^-$ ligand (see below and Fig. 2b). These results illustrate the high versatility of these polynitrile ligands, as will be further confirmed in the next sections.

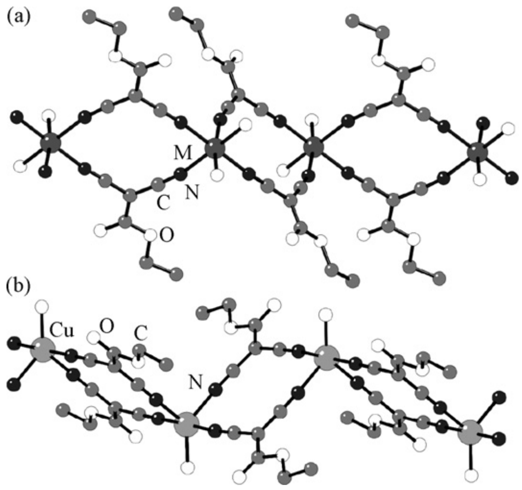


Fig. 1. (a) Chain structure in the series [M(dcnoet)$_2$(H$_2$O)$_2$] (M = Mn, Fe, Co, Ni and Zn). (b) Chain structure in the [Cu(dcnoet)$_2$(H$_2$O)] derivative.

Table 1

Compounds prepared with different metal atoms and polynitrile anions: structural types and magnetic properties.

#	Compound	Bridging mode	Structure	Magnetic coupling	Ref.
1	Mn(dcnome)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J = -0.21\ \text{cm}^{-1}$	[22]
2	Cu(dcnome)$_2$(H$_2$O)$_2$	μ_2-N,N'	2D	$J = -0.03\ \text{cm}^{-1}$	[22]
3	Mn(dcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J = -0.25\ \text{cm}^{-1}$	[18]
4	Fe(dcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J = -0.39\ \text{cm}^{-1}$	[18]
5	Co(dcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J \approx 0$	[18]
6	Ni(dcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J = -0.12\ \text{cm}^{-1}$	[18]
7	Cu(dcnoet)$_2$(H$_2$O)	μ_2-N,N'	1D	$J = -0.04\ \text{cm}^{-1}$	[18]
8	Zn(dcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	Diamagnetic	[18]
9	Mn(dcnoetOH)$_2$	μ_3-N,N',O	3D	$J = -0.13\ \text{cm}^{-1}$	[19]
10	Fe(dcnoetOH)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J = -0.54\ \text{cm}^{-1}$	[19]
11	Co(dcnoetOH)$_2$(H$_2$O)$_2$	μ_2-N,N'	2D	$J \approx 0$	[19]
12	Cu(dcnoetOH)$_2$	μ_3-N,N',O	3D	$J = -0.92\ \text{cm}^{-1}$	[19]
13	Mn(tcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J \approx 0$	[23]
14	Fe(tcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J \approx 0$	[23a]
15	Co(tcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J \approx 0$	[23a]
16	Cu(tcnoet)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J \approx 0$	[23a]
17	Mn(N,O-tcnopr3OH)$_2$(H$_2$O)$_2$	μ_2-N,O	1D	$\lvert D \rvert = 0.63\ \text{cm}^{-1}$	[20]
18	Fe(N,O-tcnopr3OH)$_2$(H$_2$O)$_2$	μ_2-N,O	1D	$J \approx 0$	[24]
19	Fe(N,N'-tcnopr3OH)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J \approx 0$	[24]
20	Co(N,N'-tcnopr3OH)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J \approx 0$	[20]
21	Ni(N,N'-tcnopr3OH)$_2$(H$_2$O)$_2$	μ_2-N,N'	1D	$J \approx 0$	[20]
22	Cu(N,O-tcnopr3OH)$_2$(H$_2$O)$_2$	μ_2-N,O	1D	$J = -0.01\ \text{cm}^{-1}$	[20]
23	Cu(tcno)(H$_2$O)$_2$	μ_3-N,N',N''	1D	$J \approx 0$	[21]
24	Cu(tcpd)(H$_2$O)$_2$	μ_4-N,N',N'',N'''	3D	$J = 0.42\ \text{cm}^{-1}$	[25]

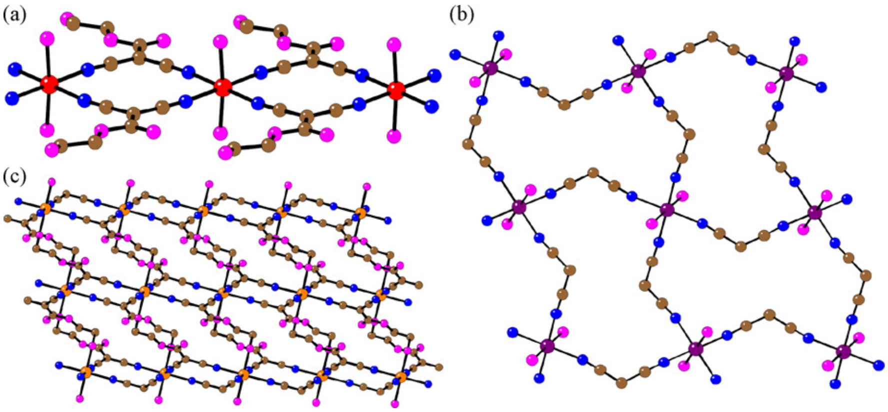


Fig. 2. (a) Chain structure in compound [Fe(dcnoetOH)$_2$(H$_2$O)$_2$]. (b) Layered structure in compound [Co(dcnoetOH)$_2$(H$_2$O)$_2$]. (For clarity, only the "NC–C–CN" bridges are drawn.) (c) 3D structure in compound [Mn(dcnoetOH)$_2$] showing the inter-planar connexions. Colour code: Fe = red, Co = violet, Mn = orange, C = brown, N = blue and O = pink.

2.1.1.2. dcnoetOH$^-$ ([(NC)$_2$CC(O)OEtOH]$^-$) with Mn(II), Fe(II), Co(II) and Cu(II). This polynitrile ligand is very similar to the previous one but shows an additional potential coordinating group since the –CH$_2$–CH$_3$ group has been substituted by a –CH$_2$–CH$_2$OH group. This novel polynitrile ligand provides a clear example of how the extra coordinating group may affect the coordination of the ligand and, therefore, the final structure of the compounds (as observed in the Mn(II) (**9**) and Cu(II) (**12**) derivatives, where the ligand also coordinates through its –OH group). Furthermore, even in those cases [M = Fe(II) (**10**) and Co(II) (**11**)] where the coordination of the ligand is similar to that observed in the related dcnoet$^-$ ligand, the extra –OH group plays a steric role that modifies the final structure. Thus, when the dcnoetOH$^-$ ligand is combined with Fe(II) it affords a 1D compound (Fig. 2a), whereas with Co(II) it forms a 2D compound (Fig. 2b), both formulated as [M(dcnoetOH)$_2$(H$_2$O)$_2$]. Interestingly, with Mn(II) and Cu(II) the water molecules are removed to form two isostructural 3D compounds formulated as [M(dcnoetOH)$_2$] (Fig. 2c) [19]. Although in both Fe(II) derivatives (compounds **4** and **10**, Figs. 1a and 2a, respectively), the ligands (dcnoet$^-$ and dcnoetOH$^-$) present the same *N*,*N*′ coordination mode, in the dcnoetOH$^-$ compound (**10**) the 12-membered dimetallacycles are co-planar, giving rise to a flat ribbon formed by co-planar cycles (Fig. 2a) instead of a zigzag chain as in the dcnoet$^-$ derivative (Fig. 1a). This is due to the fact that the four ligands connected to the Fe(II) metals leave two *trans* free positions (which are occupied by two water molecules). In contrast, in the dcnoet$^-$ derivatives the two water molecules are located in *cis*. A possible reason to explain this difference is the steric effect played by the OH group of the dcnoetOH$^-$ ligand since the disposition shown by the dcnoetOH$^-$ derivative implies a bigger inter-ligand distance. The Co(II) and Fe(II) derivatives present the same formula but the coordination mode of the ligand is different. Thus, in the Co(II) derivative the metal ions are connected to four different dcnoetOH$^-$ ligands and the ligands also bridge two metal atoms but the bridges between the Co(II) ions are single "NC–C–CN" bridges instead of double ones as observed in the Fe(II) compound (Fig. 2a and b). This 4:2 connectivity leads to two-dimensional rectangular planes, as shown in Fig. 2b. Finally, the Mn(II) and Cu(II) derivatives show a different coordination mode where the ligand now acts as a μ_3-bridge coordinating the metal atoms through the two –CN groups and also through the extra –OH group. This μ_3 connectivity implies a higher dimensionality (3D) in these two compounds. The 3D structure can be described as rectangular layers (similar to those displayed by the Co(II) derivative) that are interconnected through the –OH groups (Fig. 2c). A possible reason to explain this important difference found in the coordination mode of the ligand may be the bigger size of the Mn(II) ion compared to the Fe(II) and Co(II) ions. This bigger size would allow the –OH group to link the Mn(II) ion but neither the Fe(II) nor the Co(II) ions. In the case of the Cu(II) derivative this difference could be explained by the larger flexibility of the Cu(II) coordination sphere. In fact, the Cu(II) derivative presents a marked Jahn–Teller effect where the oxygen atom of the –OH group of the ligand occupies the elongated positions of the distorted octahedron. The magnetic properties show, as in the previous series, the presence of very weak antiferromagnetic couplings in all the cases that are easily reproduced with a regular chain model for the Fe(II) derivative and with a quadratic layer antiferromagnet (QLAF) model for the Mn(II) and Cu(II) derivatives since the long interlayer connections can be neglected [19].

2.1.2. Tetranitrile ligands

2.1.2.1. tcnoet$^-$ ([(NC)$_2$CC(OEt)C(CN)$_2$]$^-$) with Mn(II), Fe(II), Co(II) and Cu(II). This polynitrile ligand presents four –CN groups since the terminal oxo group present in the dcnoet$^-$ ligands (see above) has been replaced by a –C(CN)$_2$ group. This polynitrile anion has been used with Mn(II), Fe(II), Co(II) and Cu(II) to afford the series of isostructural compounds formulated as [M(tcnoet)$_2$(H$_2$O)$_2$] with M = Mn(II) (**13**), Fe(II) (**14**), Co(II) (**15**) and Cu(II) (**16**) [23]. This series exhibits an original 1D structure generated by large 16-membered dimetallacycles formed by two metal atoms connected through two different polynitrile ligands. Each ligand coordinates to two different metal ions through two –CN groups of two different –C(CN)$_2$ wings (Fig. 3) and each metal atom presents an octahedral MN$_4$O$_2$ coordination geometry formed by four different tcnoet$^-$ ligands and two *trans* water molecules. The resulting chains are connected each other by H-bonds to generate an overall 3D structure. All the compounds of this family are paramagnetic, as expected from the long double NC–CCC–CN bridges connecting the metal atoms (with M–M distances of 9.017 Å in **13**, 8.887 Å in **15** and 9.133 Å in **16**).

2.1.2.2. tcnopr3OH$^-$ ([(NC)$_2$CC(O(CH$_2$)$_3$OH)C(CN)$_2$]$^-$) with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II). This polynitrile ligand presents four –CN groups since the terminal oxo group present in the dcnoet$^-$

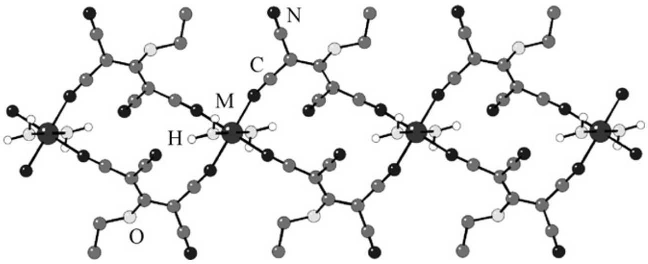


Fig. 3. Chain structure of the series of compounds [M(tcnoet)$_2$(H$_2$O)$_2$].

and dcnoetOH$^-$ ligands (see above) has been replaced by a –C(CN)$_2$ group. Besides these four coordinating groups, this ligand possesses an additional –CH$_2$–CH$_2$–CH$_2$OH coordinating group, rendering this polynitrile a potentially penta-coordinating ligand. As a consequence of this multiple coordinating modes, this ligand has afforded two different series of compounds with the same formula when combined with the first row transition metals. Furthermore, in the case of the Fe(II) derivative, this ligand has given rise to a couple of linkage isomers in a chain compound which is, as far as we know, the first example of linkage isomerism in a chain compound [24]. When combined with Mn(II), Fe(II) and Cu(II), this ligand acts as a *N*,*O*-coordinating ligand to yield the series of compounds [M(*N*,*O*-tcnopr3OH)$_2$(H$_2$O)$_2$] with M = Mn(II) (**17**), Fe(II) (**18**) and Cu(II) (**22**), whereas with Co(II), Ni(II) and Fe(II) it acts as a *N*,*N*′-coordinating ligand to yield the series of compounds formulated as [M(*N*,*N*′-tcnopr3OH)$_2$(H$_2$O)$_2$] with M = Fe(II) (**19**), Co(II) (**20**) and Ni(II) (**21**) [20]. Both series present quite similar chain structures with double polynitrile bridges connecting the metal atoms. The main difference between both structures is the coordination mode of the ligand. In the *N*,*O*-isomers, the ligand coordinates one metal atom through a –CN group and through the oxygen atom of the –(CH$_2$)$_3$OH group (Fig. 4a) whereas in the *N*,*N*′-isomer, the ligand coordinates the metal atoms through two –CN groups to form, in both cases, 1D chains with double polynitrile bridges between the metals (Fig. 4b). The difference of the *N*,*N*′-isomer with other chain structures observed in the dicyano ligands is that now the two –CN groups coordinated to the metals belong to different –C(CN)$_2$ wings and, therefore, the bridge connecting the metal atoms (NC–CCC–CN) is much longer (Fig. 4b). As in the case of the dcnoetOH$^-$ ligand, it seems that the size of the metal atom is again the most important factor determining the favoured isomer. Thus, for the bigger Mn(II) ion and for the less rigid Cu(II) ion, the polynitrile ligand adopts the *N*,*O*-coordination mode whereas for the smaller Co(II) and Ni(II) metal ions the ligand adopts the *N*,*N*′-coordination mode. Interestingly, the size of the Fe(II) ion is in between Mn(II) and Co(II) and to date is the only one that forms both type of isomers, by slightly changing the synthetic conditions. Given the very long bridges connecting the metal atoms in both isomers, it is not surprising that the magnetic measurements show a paramagnetic behaviour for all the compounds [20].

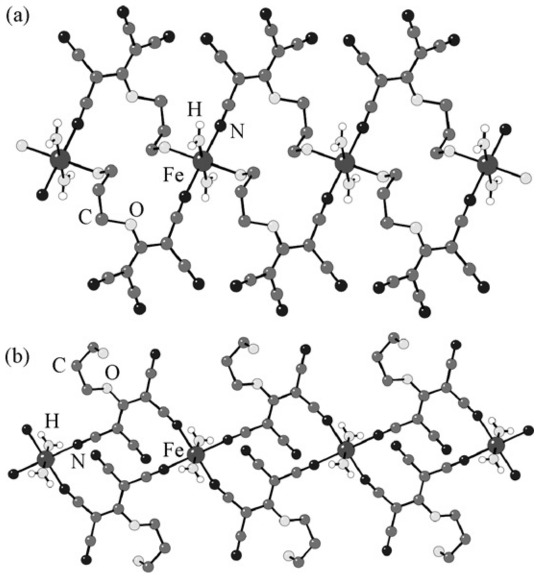


Fig. 4. Chain structure of (a) the *N*,*O*-isomer and (b) the *N*,*N*′-isomer of the compound Fe(tcnopr3OH)$_2$(H$_2$O)$_2$.

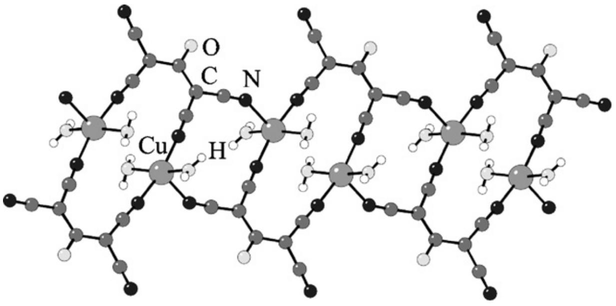


Fig. 5. Alternating chain structure of compound Cu(tcno)(H$_2$O)$_2$.

2.1.2.3. *tcno^{2-} ([(NC)$_2$CC(O)C(CN)$_2$]$^{2-}$) with Cu(II).* This polynitrile ligand possesses a terminal oxygen atom without any alkyl or alkoxo group (as the dcnoet$^-$ ligand) and has four terminal –CN groups with a total anionic charge of −2. These two particularities (presence of an anionic terminal oxo group and a −2 anionic charge) render this ligand especially original. These particularities may explain why only the Cu(II) ion has afforded a coordination compound with this ligand [21]. This compound, formulated as Cu(tcno)(H$_2$O)$_2$ (**23**) presents a chain structure with alternating double polynitrile bridges. Each Cu(II) ion has a CuN$_3$O$_2$ square pyramidal geometry with three N atoms from three different tcno^{2-} ligands and two water molecules (Fig. 5). The alternating chain presents two types of bridges: a double “NC–C–CN” bridge (forming 12-membered dimetallacycles) and a longer double NC–CCC–CN bridge (forming 16-membered dimetallacycles). Albeit, the metal–metal distances through the long bridges (3.644 Å) are much shorter than the ones through the shorter bridges (7.881 Å) since the long bridges concern –CN groups in *cis* positions. The ligand presents an unusual μ_3-bridging mode (when compared with other polynitrile ligands without aromatic character), probably due to the high charge of the ligand (−2 compared to −1 for most of the polynitrile ligands). The magnetic properties show that both types of bridges are not able to transmit any magnetic coupling and, therefore, compound Cu(tcno)(H$_2$O)$_2$ is essentially paramagnetic.

2.1.3. Hexanitrile ligands

2.1.3.1. *tcpd^{2-} (C[C(CN)$_2$]$_3$$^{2-}$) with Cu(II).* This polynitrile ligand presents up to six –CN groups since the additional group (–O–R or –O) present in the tetracyano ligands of the previous section has been replaced by a third –C(CN)$_2$ wing to generate a dianionic ligand with approximate three fold symmetry (Scheme 1). As in the case of the parent dianion already mentioned above (tcno^{2-}), the use of the tcpd^{2-} ligand alone has only afforded a compound with Cu(II) [25]. This compound, formulated as [Cu(tcpd)(H$_2$O)$_2$]$_n$, (**24**) presents a very original 3D structure (Fig. 6) where each Cu(II) ion has an elongated octahedral CuO$_2$N$_4$ coordination formed by two *trans* water molecules and four different tcpd^{2-} anions in equatorial positions. Each ligand coordinates to four different Cu(II) ions to generate a 3D structure. This structure can be easily described as formed by two different, almost orthogonal, chains of 12-membered dimetallacycles (where the Cu(II) centres are connected through “NC–C–CN” bridges, similar to those already observed in other polynitrile ligands) that are further linked through the polynitrile ligands to form the 3D structure depicted in Fig. 6. The magnetic properties are quite surprising since this compound shows a weak, although noticeable, ferromagnetic coupling that can be well reproduced with a simple ferromagnetic chain model (with J = +0.6 K) since the most important interaction is the intra-chain one, being the inter-chain interaction negligible [25].

2.2. M:L:L′ ternary systems (L′ = co-ligand)

Besides all the above mentioned complexes prepared with polynitrile anions as ligands (together with coordinated water molecules in most cases), there are also several complexes where the polynitrile anions are not alone but contain a co-ligand that helps in the construction of the polymeric architectures. The co-ligands used are neutral and concern essentially N-donating ligands based on aromatic amines, as 2,2′-bipyridine (2,2′-bpy), 4,4′-bipyridine (4,4′-bipy) and 2,2′-bipyrimidine (2,2′-bpym) or linear di-amines as ethylenediamine (en) and 1,3-diaminopropane (tn) (Scheme 2). Interestingly, in some cases, the presence of these co-ligands significantly affects the coordination mode of the polynitrile ligand that now become terminal in some cases (Table 2) due to the competition between both ligands to coordinate the metal atoms.

2.2.1. Aromatic nitrogen donors

2.2.1.1. Bipyridine-type ligands. The 2,2′-bipyridine (2,2′-bpy) and 4,4′-bipyridine (4,4′-bpy) ligands (Scheme 2) have been very extensively used as ligands alone or in combination with many other different co-ligands. In the case of the 2,2′-bpy ligand, this fact is probably due to the chelating character of the 2,2′-bpy, that enhances the stability of its complexes with transition metal ions [26]. A recent revision of the CCDC database shows that there are almost 5000 compounds where the 2,2′-bpy ligand chelates a metal ion: one-fifth of these complexes are formed with copper and another fifth with Mn, Fe, Co or Ni; the three fifths remaining are complexes with other metals. The 4,4′-bpy has also been extensively used (although not as much as the 2,2′ isomer) mainly as a linear rod, given the disposition of the two potentially coordinating N-donor atoms. Thus, the CCDC database shows ca. 1600 complexes where the 4,4′-bpy ligand bridges two metal ions. Almost one-third are Cu(II) complexes, and another third corresponds to complexes with Mn, Fe, Co or Ni. The remaining third corresponds to complexes with other metal atoms [27].

The 2,2′-bpy ligand has only been combined with the tcnoet$^-$ polynitrile anions as co-ligand [28], and in this case, besides the tcnoet$^-$ and bpy ligands, there is an additional adipate ligand ($^-$OOC–$(CH_2)_4$–COO$^-$). Interestingly, the combination of these three ligands with Cu(II) affords two similar compounds with similar structures formulated as $[Cu_4(bpy)_4(adip)_3](tcnoet)_2$ (**25**) [28a] and $[Cu_4(bpy)_4(adip)_3](tcnoet)_2{\cdot}2H_2O$ (**26**) [28b] where the tcnoet$^-$ anions act as counterions. In both compounds, the presence of *syn–syn* carboxylate bridges directly connecting the Cu(II) ions, provides a weak antiferromagnetic coupling between them.

The 4,4′-bpy ligand has been only very recently be used as co-ligand with two polynitrile anions: tcnoetOH$^-$ [29] and tcnopr3OH [30]. In the first case the 4,4′-bpy and tcnoetOH$^-$ ligands have afforded three isostructural compounds that can be formulated as $[M(tcnoetOH)_2(4,4'\text{-bpy})(H_2O)_2]$ with M = Fe(II) (**27**), Co(II) (**28**) and Ni(II) (**29**) [29]. This series of compounds presents a chain structure formed by bridging 4,4′-bpy where the metal atoms are coordinated by two *trans* 4,4′-bpy, two *trans* tcnoetOH$^-$ ligands and two *trans* water molecules to form a centro-symmetric octahedral MN_4O_2 coordination geometry (Fig. 7a). All these compounds are essentially paramagnetic due to the presence of the long 4,4′-bpy bridges connecting the metal atoms.

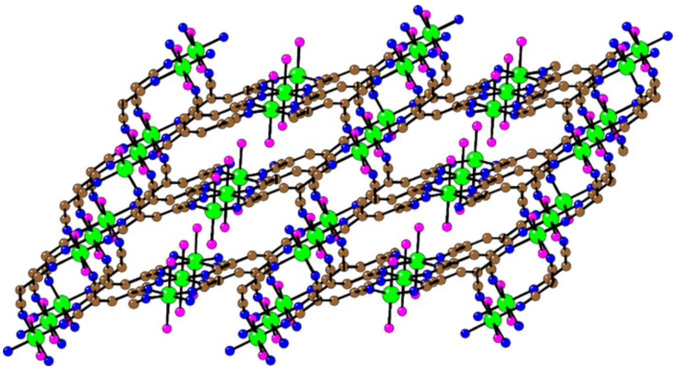


Fig. 6. 3D structure of compound $[Cu(tcpd)(H_2O)_2]_n$, showing the two orthogonal chains and the connexions between them. Colour code: Cu = green, C = brown, N = blue and O = pink.

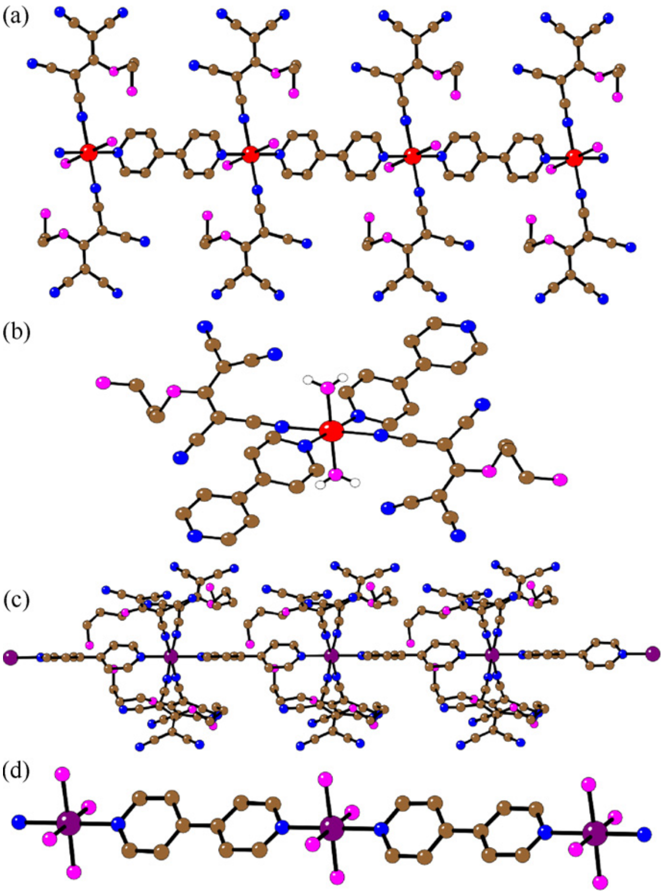
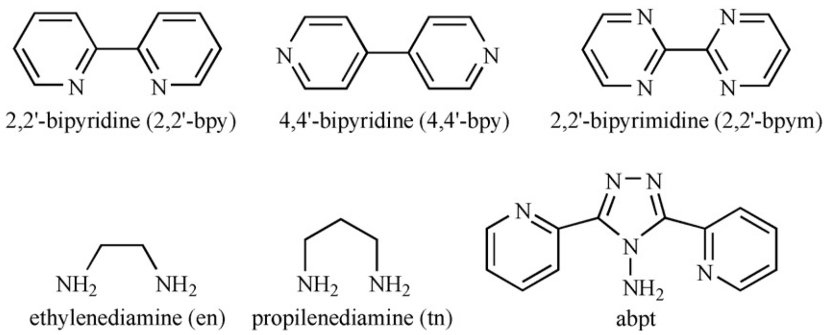


Fig. 7. 4,4′-Bipyridine and polynitrile combinations: (a) chain structure of the series $[M(tcnoetOH)_2(4,4'\text{-bpy})(H_2O)_2]$ with M = Fe, Co and Ni. (b) Discrete mononuclear complex in $[Fe(tcnopr3OH)_2(4,4'\text{-bpy})_2(H_2O)_2]$, (c) anionic chain and (d) cationic chain in the compound $[Co(tcnopr3OH)_2(4,4'\text{-bpy})(H_2O)_2]$. Colour code: Fe = red, Co = violet, C = brown, N = blue and O = pink.

The second polynitrile ligand that has been combined with 4,4′-bpy is the tcnopr3OH$^-$ anion. Interestingly, and in contrast to the tcnoetOH$^-$ ligand, the tcnopr3OH$^-$ ligand affords a molecular discrete structure with Fe(II) whereas it gives rise to a double chain structure with Co(II) (Fig. 7). The discrete structure, formulated as $[Fe(tcnopr3OH)_2(4,4'\text{-bpy})_2(H_2O)_2]$ (**30**), presents a Fe(II) ion located in an inversion centre and surrounded by two *trans* tcnopr3OH$^-$ ligands, two terminal, also in *trans*, 4,4′-bpy ligands and two water molecules forming a neutral octahedral complex (Fig. 7b). The Co(II) complex, formulated as $[Co(tcnopr3OH)_2(4,4'\text{-bpy})(H_2O)_2]$ (**31**), presents a very original structure formed by two different types of chains: an anionic one with formula $[Co(tcnopr3OH)_4(4,4'\text{-bpy})]^{2-}$ where the Co(II) ions are bridged by simple 4,4′-bpy ligands in *trans* configuration and complete their octahedral coordination with four tcnopr3OH ligands (Fig. 7c) and a cationic one, formulated as $[Co(4,4'\text{-bpy})(H_2O)_4]^{2+}$ with a similar structure to the anionic chain but with four water molecules replacing the four tcnopr3OH$^-$ ligands (Fig. 7d). The parallel cationic and



Scheme 2. Co-ligands used with polynitrile anions.

anionic chains are packed in a tetragonal way in the solid, i.e., each anionic chain is surrounded by four cationic chains and vice-versa. As expected, both compounds are paramagnetic in agreement with the long 4,4′-bpy bridges connecting the metal atoms.

2.2.1.2. 2,2′-Bipyrimidine ligand. The 2,2′-bipyrimidine (bpym) ligand (Scheme 2) has been very extensively used since it presents a double chelating coordination site that can easily bridge two different metal atoms to form magnetic polymeric structures. The CCDC database contains, to date, 169 different compounds presenting the bpym ligand with its bis-chelating coordination mode. In most of these complexes the bpym ligand bridges two identical metal atoms with Cu(II) being the most often found (representing 1/4 of the total number of complexes). From the magnetic point of view the bpym ligand is well known to transmit moderate antiferromagnetic exchange interactions with most of the transition metal atoms [31]. These properties render this ligand a good candidate to construct high dimensional magnetic structures when combined with different polynitrile ligands. In this section we will describe the examples reported to date by using bpym and diverse polynitrile ligands and we will show how the combination of both bridging ligands may generate very original compounds from both, the structural and the magnetic points of view.

The combination of dcnoet$^-$ with bpym and different transition metal ions afforded the series of compounds formulated as $[M_2(dcnoet)_4(bpym)(H_2O)_2]$ with M = Mn(II) (**32**) and Co(II) (**33**) and $[M_2(dcnoet)_4(bpym)(H_2O)_4]\cdot 2H_2O$ with M = Fe(II) (**34**) and Cu(II) (**35**) [31a]. In this series, the Mn(II) and Co(II) derivatives are isostructural and present a 2D structure formed by hexagonal rings (distorted honey-comb structure, Fig. 8a). Each metal ion is surrounded by five N atoms (three N atoms form three different dcnoet$^-$ ligands in *fac*-conformation and two from a chelating bpym ligand) and one water molecule. Two dcnoet$^-$ anions act as bridging ligands whereas a third one acts as a terminal ligand. As expected, the bpym molecule acts as bis-bidentate ligand and forms two of the six sides of the hexagonal rings in the layers. Interestingly, the Fe(II) and Cu(II) derivatives show a very different structure formed by discrete dimers generated by the bis-bidentate bpym ligand and by four terminal dcnoet$^-$ ligands (Fig. 8b). This important structural difference arises from the coordination mode of the polynitrile ligands and shows the rich diversity of coordination modes and structural motives that can generate. The magnetic properties in both series were satisfactorily reproduced with a simple dimer model since the coupling through the long polynitrile bridges in the Mn(II) derivative can be neglected. As expected, the Mn(II) and Fe(II) derivatives show weak antiferromagnetic interactions whereas the Cu(II) derivative shows much more stronger antiferromagnetic coupling.

Two closely related ligands that have also been combined with bpym and Cu(II) ions are the tcnome$^-$ [32] and tcnoet$^-$ anions [33]. The two compounds so obtained can be formulated as $[Cu(bpym)(tcnome)_2]\cdot H_2O$ (**36**) and $[Cu(bpym)(tcnoet)_2]\cdot H_2O$ (**37**) and present the same chain structure where the Cu(II) ions are bridged though the bpym ligands (Fig. 9a).

Each Cu(II) ion presents a distorted octahedral CuN_6 coordination geometry formed by four N atoms from two bpym ligands (that bridge the Cu(II) ions with its neighbours in the chain) and two N atoms from two terminal tcnoR$^-$ ligands (R = me and et) [33]. The tcnoet$^-$ compound presents several very interesting facts: (i) the two tcnoet$^-$ ligands are located in *cis* positions and, there-

Table 2
Series prepared with transition metal ions, polynitrile anions and neutral co-ligands: structural types and magnetic properties.

#	Compound	Co-ligand	Polynitrile coord. mode	Structure	Magnetic properties	Ref.
25	$[Cu_4(2,2'\text{-bpy})_4(adip)_2](tcnoet)_2$	2,2′-bpy	Isolated	1D	$J = -7.74\ cm^{-1}$	[28a]
26	$[Cu_4(2,2'\text{-bpy})_4(adip)_3](tcnoet)_2\cdot 2H_2O$	2,2′-bpy	Isolated	1D	$J = -3.26\ cm^{-1}$	[28b]
27	$[Fe(tcnoetOH)_2(4,4'\text{–bpy})(H_2O)_2]$	4,4′-bpy	*N*-terminal	1D	$\|D\| = 3.07\ cm^{-1}$	[29]
28	$[Co(tcnoetOH)_2(4,4'\text{-bpy})(H_2O)_2]$	4,4′-bpy	*N*-terminal	1D	$J \approx 0$	[29]
29	$[Ni(tcnoetOH)_2(4,4'\text{-bpy})(H_2O)_2]$	4,4′-bpy	*N*-terminal	1D	$\|D\| = 8.33\ cm^{-1}$	[29]
30	$[Fe(tcnopr3OH)_2(4,4'\text{–bpy})_2(H_2O)_2]$	4,4′-bpy	*N*-terminal	Monomer	$J \approx 0$	[30]
31	$[Co(tcnopr3OH)_2(4,4'\text{-bpy})(H_2O)_2]$	4,4′-bpy	*N*-terminal	Two-1D	$J \approx 0$	[30]
32	$[Mn_2(dcnoet)_4(bpym)(H_2O)_2]$	2,2′-bpym	μ_2-*N*,*N*′ + *N*-terminal	2D	$J = -0.60\ cm^{-1}$	[31a]
33	$[Co_2(dcnoet)_4(bpym)(H_2O)_2]$	2,2′-bpym	μ_2-*N*,*N*′ + *N*-terminal	2D	$J \approx 0$	[31a]
34	$[Fe_2(dcnoet)_4(bpym)(H_2O)_4]\cdot 2H_2O$	2,2′-bpym	*N*-terminal	Dimer	$J = -1.5\ cm^{-1}$	[31a]
35	$[Cu_2(dcnoet)_4(bpym)(H_2O)_4]\cdot 2H_2O$	2,2′-bpym	*N*-terminal	Dimer	$J = -99.0\ cm^{-1}$	[31a]
36	$[Cu(bpym)(tcnome)_2].H_2O$	2,2′-bpym	*N*-terminal	1D	$J = -53\ cm^{-1}$	[32]
37	$[Cu(bpym)(tcnoet)_2]\cdot H_2O$	2,2′-bpym	*N*-terminal	1D	$J = -0.50\ cm^{-1}$ $J' = 2.43\ cm^{-1}$	[33]
38	$[Cu_2(bpym)(tcpd)_2(H_2O)_4]\cdot 2H_2O$	2,2′-bpym	μ_2-*N*,*N*′	1D	$J = -90\ cm^{-1}$	[34]
39	$[Mn_2(bpym)_3(tcpd)_2(H_2O)_2]$	2,2′-bpym	*N*-terminal	Dimer	$J = -0.58\ cm^{-1}$	[35]
40	$[Cu(tcpd)(en)]$	en	μ_4-*N*,*N*′,*N*″,*N*‴	3D	$J \approx 0$	[25]
41	$[Cu(tcpd)(en)_2]$	en	μ_2-*N*,*N*′	1D	$J \approx 0$	[36]
42	$[Cu(tcpd)(tn)]$	tn	μ_4-tcpd *N*,*N*′,*N*″,*N*‴	3D	$J = -0.07\ cm^{-1}$	[34,37]
43	$[Cu(tcpd)(tn)_2]\cdot H_2O$	tn	μ_2-*N*,*N*′	1D	$J = -0.18\ cm^{-1}$	[34]

fore, the Cu–bpym–Cu units are not co-planar along the chain. (ii) The Cu–N bond distances at room temperature deviate from the usual elongated octahedron due to the Jahn–Teller distortions. This unusual distortion generates a dynamic pseudo Jahn–Teller distortion when cooling down the compound that generates a quite unusual thermo-chromic transition (Fig. 9c). (iii) Even more interesting is the presence of a structural transition at ca. 30 K that leads to a magnetic transition with a small hysteresis of ca. 2 K (Fig. 9c). This transition implies that below ca. 30 K there are two crystallographically different bpym ligands in the chain (above 30 K all the bpym bridges are identical) and leads to a dimerization of the chain (Fig. 9b) that passes from a paramagnetic behaviour to an antiferromagnetic one. In agreement with detailed crystallographic studies at helium temperature, DFT calculations confirm and explain this abrupt transition as a result of the changes in the Cu–N bond distances [33].

The last polynitrile used with the bpym ligand is the tcpd^{2-} dianion, that has been used with Cu(II) and Mn(II) to form the compounds $[Cu_2(bpym)(tcpd)_2(H_2O)_4]\cdot 2H_2O$ (**38**) [34] and $[Mn_2(bpym)_3(tcpd)_2(H_2O)_2]$ (**39**) [35]. The Cu(II) compound has an alternating chain structure where the Cu(II) ions are alternatively connected through bis-bidentate bpym ligands and through double "NC–C–CN" bridges of the tcpd^{2-} ligand (Fig. 10a). Each Cu(II) ion is thus, connected to two N atoms from a chelate bpym molecule, two N atoms from two different tcpd^{2-} ligands and two water molecules in *trans* positions. As expected from the structure, the magnetic properties can be well reproduced with a dimer model since the magnetic coupling through the double "NC–C–CN" bridges is much weaker than the coupling through the bis-bidentante bpym ligand.

The Mn(II) derivative, $[Mn_2(bpym)_3(tcpd)_2(H_2O)_2]$, presents a dimeric centro-symmetric structure with a bis-bidentate bpym ligand bridging the Mn(II) centres. Each Mn(II) centre is also coordinated to a terminal chelating bpym ligand, a terminal tcpd^{2-} ligand and a water molecule (Fig. 10b). The magnetic properties show the presence of a weak antiferromagnetic interaction between the two Mn(II) ions, as expected for a bis-bidentate bpym bridge.

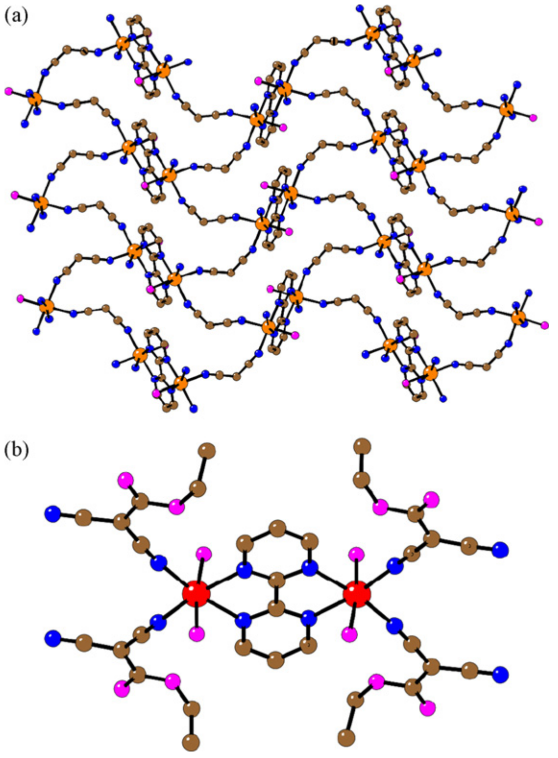


Fig. 8. Structure of (a) the 2D network in compounds $[M_2(bpym)(dcnoet)_4(H_2O)_2]$ (M = Mn and Co). Only the NC–C–CN bridges of the dcnoet$^-$ ligand are shown for clarity. (b) Discrete dimers in $[Fe_2(bpym)(dcnoet)_4(H_2O)_4]\cdot 2H_2O$. Colour code: Fe = red, Co = violet, C = brown, N = blue and O = pink.

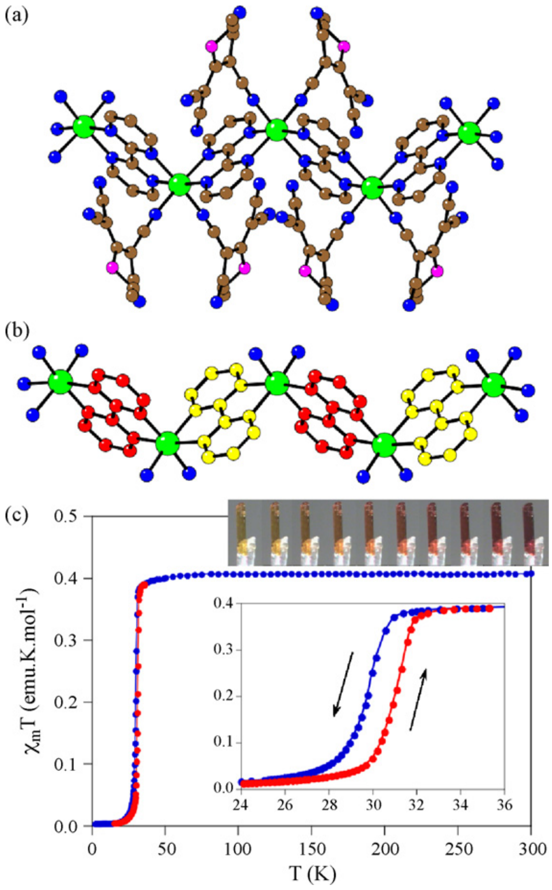


Fig. 9. (a) Chain structure at room temperature of the [Cu(bpym)(tcnoet)] compound. (b) Structure of the same compound at 10 K showing the two crystallographically different bpym bridges (in red and yellow). (c) Magnetic properties of the same compound showing the abrupt magnetic transition at ca. 30 K. Inset: pictures of a single crystal showing the thermo-chromic transition in the 300–100 K range. Colour code in figure (a): Cu = green, C = brown, N = blue and O = pink.

2.2.2. *Aliphatic nitrogen donors*

In addition to the aromatic amines bipyridine and bipyrimidine, two aliphatic linear di-amines as ethylenediamine (en) and 1,3-diaminopropane (tn) (Scheme 2) have also been used as co-ligands with the tcpd^{2-} polynitrile ligand. Interestingly, both ligands have been combined with Cu(II) and in both cases two different compounds are obtained. Thus, when the tcpd^{2-} and en ligands are combined with Cu(II), two compounds formulated as $[Cu(tcpd)(en)]_n$ (**40**) [25] and $[Cu(tcpd)(en)_2]_n$ (**41**) [36] have been obtained. Compound $[Cu(tcpd)(en)]_n$ (**40**) involves μ_4-tcpd^{2-} bridging ligands connecting the Cu(II) centres in a sophisticated 3D structure (Fig. 11a). Each Cu(II) atom has a distorted CuN_6 octahedral coordination geometry formed by four N atoms from four tcpd^{2-} ligands and two N atoms from a chelating en co-ligand. Since all the bridges connecting the Cu(II) ions ("NC–C–CN" or "NC–CCC–CN" bridges) in this complex are long, this compound behaves as a paramagnet in the whole temperature range studied [25].

Compound $[Cu(tcpd)(en)_2]_n$ (**41**) presents a chain structure where the Cu(II) ions are connected through μ_2-tcpd^{2-} bridges and each Cu(II) ion presents an elongated CuN_6 octahedral coordination geometry formed by the two *trans* bridging tcpd^{2-} ligands and by two chelating en co-ligands (Fig. 11b). As expected from the long

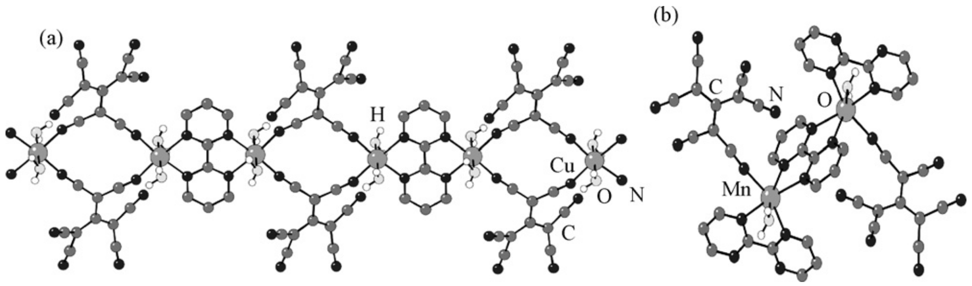


Fig. 10. (a) Chain structure of compound $[Cu_2(bpym)(tcpd)_2(H_2O)_4]\cdot 2H_2O$ showing the alternating bpym and $tcpd^{2-}$ bridges. (b) Dimeric structure of compound $[Mn_2(bpym)_3(tcpd)_2(H_2O)_2]$.

"NC–CCC–CN" bridge connecting the Cu(II) ions, this compound is paramagnetic in the temperature range 300–2 K [36].

The other linear di-amine ligand used as a co-ligand is the related 1,3-diaminopropane (tn) ligand. This ligand, together with $tcpd^{2-}$ combined with Cu(II), afforded two different compounds formulated as [Cu(tcpd)(tn)] (**42**) [34,37] and $[Cu(tcpd)(tn)_2]\cdot H_2O$ (**43**) [34]. Although both compounds are obtained in the same synthesis, it was possible to modify the synthetic procedure to obtain compound **43** as a pure product but this was not possible for compound **42**. The structure of [Cu(tcpd)(tn)] (**42**) shows a μ_4-$tcpd^{2-}$ ligand that bridges four Cu(II) ions with four different –CN groups (two from one $-C(CN)_2$ wing and one from each of the two remaining $-C(CN)_2$ wings, Fig. 11c). Each Cu(II) ion presents an elongated CuN_6 octahedral coordination geometry with four N atoms from four different $tcpd^{2-}$ ligands and two N atoms form a chelating tn co-ligand. In spite of using a chelating ligand (tn) instead of a bridging one (as 4,4′-bpy and 2,2′-bpym), the μ_4-bridging mode of the $tcpd^{2-}$ ligand and the coordination number of the Cu(II) ions (six) leads to a sophisticated 3D structure as depicted in Fig. 11c. It is interesting to note that this structure is equivalent to the one observed in the related compound [Cu(tcpd)(en)]. The only difference is the presence of a longer $Cu–N_{(tcpd)}$ bond distance (ca. 2.7 Å in the tn compound, vs. 2.4 Å in the en compound) that can be attributed to the steric effect of the bigger tn ligand as compared with the en one. As expected from the long "NC–C–CN" and "NC–CCC–CN" bridges, and as also observed in the related en derivative, this compound is essentially paramagnetic and presents a very weak antiferromagnetic coupling through the shorter "NC–C–CN" bridges that can be well reproduced with a regular chain model [34].

The second compound formed by combining Cu(II), $tcpd^{2-}$ and tn, $[Cu(tcpd)(tn)_2]\cdot H_2O$ (**43**) presents a chain structure where the Cu(II) ions are connected by μ_2-bridging $tcpd^{2-}$ ligands (Fig. 11d). The coordination around the Cu(II) ions is completed by two chelating tn ligands to generate an elongated CuN_4N_2 octahedral geometry. The magnetic properties in this compound can be well reproduced with an S = 1/2 regular chain model with very low coupling constants, in agreement with the chain structure and the

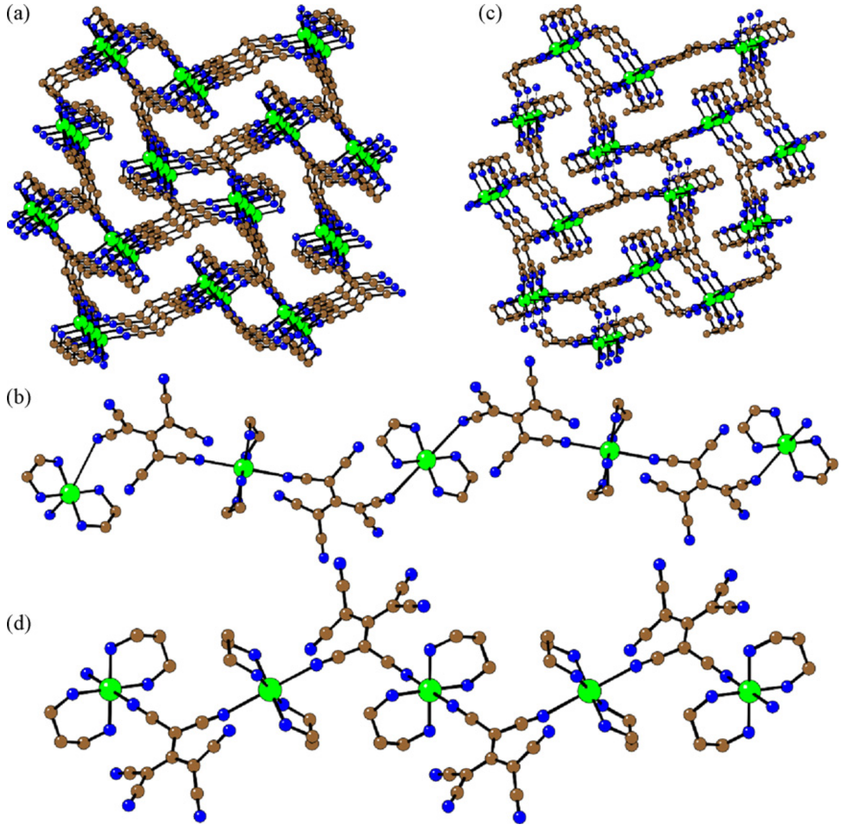


Fig. 11. (a) 3D structure of compound $[Cu(tcpd)(en)]_n$ (b) Chain structure of compound $[Cu(tcpd)(en)_2]_n$. (c) 3D structure of compound [Cu(tcpd)(tn)]. (d) Chain structure of compound $[Cu(tcpd)(tn)_2]\cdot H_2O$. Colour code: Cu = green, C = brown, N = blue and O = pink.

long “NC–C–CN” bridges [34]. As in the case of the 3D compounds based on en and tn co-ligands, their corresponding 1D compounds also present the same chain structure with a similar distribution of the ligands. The only difference is the relative position of the bridging –CN groups: they belong to the same $-\mathrm{C(CN)_2}$ wing in the tn derivative and to different $-\mathrm{C(CN)_2}$ wings in the en one (Fig. 11).

3. Concluding remarks and perspectives

The polynitrile anions have demonstrated to be a very useful tool for the design and synthesis of diverse structural architectures from discrete molecules to mono-, bi- and tri-dimensional structures. In most compounds, the polynitrile anions have shown their ability to coordinate different metal atoms and to act as bridges connecting two or more metal ions. This empirical fact can be anticipated from two special characteristics of the polynitrile anions: (i) they present several potentially coordinating groups (mainly –CN groups) and (ii) the impossibility to act as a chelating ligand since the consecutive –CN groups are rigid and point toward different positions. Moreover, they have also shown their ability to coordinate metal atoms in the presence of other co-ligands (either bridging or chelating) to construct original architectures. Furthermore, as described in this issue, the ability of such ligand to act with several coordination modes and also to increase the ligand field strength has been used to tune the ligand field strength to design new complexes presenting spin crossover (SCO) transitions. A nice example of this ability is formed by the extended series of neutral complexes prepared with Fe(II), abpt (=4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) and different polynitrile ligands. In this series, formulated as $[\mathrm{Fe(abpt)_2X_2}]$ (X = tcm$^-$, tcnome$^-$, tcnoet$^-$, tcnopr$^-$, tcnoetOH$^-$, tncopr3OH$^-$, tcnopr2OH$^-$ and tcnsme$^-$), the enhancement of the ligand field strength has led to SCO transitions at temperatures even above room temperature [38,39] as described in detail in another contribution in this issue. Furthermore, the use of a dianionic polynitrile ligand with up to six potentially coordinating groups, as the tcpd^{2-}, in combination with Fe(II) and the abpt co-ligand, has led to the first chain compound with a cyanocarbanion presenting a spin crossover transition [40].

A further advantage of the polynitrile anions is the possibility to be reduced or oxidized to generate neutral or dianionic radicals that, besides their high ability to coordinate and bridge metal atoms, can transmit the magnetic coupling between them in a much more effective way. Attempts to prepare metal complexes with polynitriles using electrochemical and chemical redox processes are underway.

Acknowledgements

We acknowledge the European Union (COST Action D35-WG11 and MAGMANet network of excellence), the CNRS, Brest University, the French Ministère de la Recherche and Ministère des Affaires Etrangères et Europénnes (TASSILI PHC Project 08MDU732), the Spanish Ministerio de Educación y Ciencia (Projects MAT2007-61584, and CSD 2007-00010 Consolider-Ingenio in Molecular Nanoscience) and the Generalitat Valenciana (Project PROMETEO/2009/095) for financial support.

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