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New coordination polymers with a 2,2-dicyano-1-ethoxyethenolate (dcne$^-$) bridging ligand: syntheses, structural characterisation and magnetic properties of [M(dcne)$_2$(H$_2$O)$_2$] (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Zn^{II}) and [Cu(dcne)$_2$(H$_2$O)]

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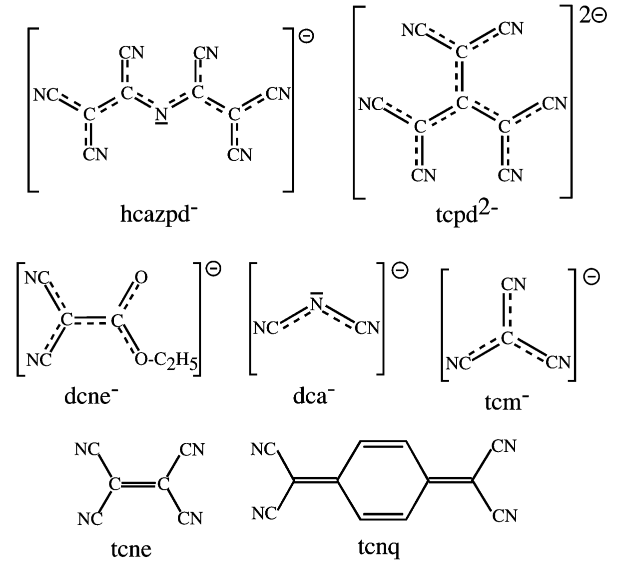
New polymeric materials [M(dcne)$_2$(H$_2$O)$_2$] with M = Mn^{II} (**1**), Fe^{II} (**2**), Co^{II} (**3**), Ni^{II} (**4**) and Zn^{II} (**5**) and [Cu(dcne)$_2$(H$_2$O)] (**6**) (dcne$^-$ = [(CN)$_2$CC(O)OEt)]$^-$ = 2,2-dicyano-1-ethoxyethenolate anion) have been synthesised and characterised by infrared spectroscopy, X-ray crystallography and magnetic measurements. In these compounds, each organic ligand acts in a bridging mode with its two nitrogen atoms bound to two different metal cations. In compounds **1**–**5**, each metal cation has a pseudo-octahedral *cis*-MN$_4$O$_2$ environment with four nitrogen atoms from four different organic ligands and two oxygen atoms from two water molecules. In compound **6**, only one water molecule is coordinated and each copper(II) cation presents a CuN$_4$O distorted trigonal bipyramid environment with a perfectly planar CuN$_2$O equatorial plane. In all compounds the molecular arrangement involves 12-membered M(dcne)$_2$M dimetallacycles that share a M atom forming chains running along the [101] direction with alternated, almost orthogonal, dimetallacycles. The intra-chain M ··· M distances (7.4270(2) Å in **3**, 7.4628(2) Å in **5** and 7.2299(3) Å in **6**) are longer than the inter-chain ones (6.0430(4) Å in **3**, 6.0907(3) Å in **5** and 5.9648(5) Å in **6**). The chains are connected by hydrogen bonds between the coordinated water molecules and the terminal oxygen atom of the organic ligand, giving rise to a 3D structure. Magnetic measurements show very weak antiferromagnetic coupling between metal centres that can be satisfactorily reproduced with a regular antiferromagnetic classical spin chain model.

Introduction

In the last few years, cyano- and azacyano-carbanions have received considerable interest in the field of coordination chemistry and molecular materials.[1–9] The dicyanamide anion (N(CN)$_2^-$ = dca$^-$) and related cyano- or azacyano-carbanions such as the tricyanomethanide anion ([C$_4$N$_3$]$^-$ = [C(CN)$_3$]$^-$ = tcm$^-$), the 1,1,2,4,5,5-hexacyano-3-azapenta-1,4-dienide anion ([C$_{10}$N$_7$]$^-$ = ([C(CN)$_2$C(CN)]$_2$N)$^-$ = hcazpd$^-$) and the 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide anion ([C$_{10}$N$_6$]$^{2-}$ = (C[C(CN)$_2$]$_3$)$^{2-}$ = tcpd^{2-}) (Scheme 1) are interesting ligands due to their high electronic delocalization and their cyano groups juxtaposed in such a way that they cannot all coordinate to the same metal ion. These organic anionic ligands adopt different bridging coordination modes which afford fascinating molecular structures of different dimensionalities and unusual magnetic properties.[1,4–9] For the binary systems ML$_n$, many extended polymeric compounds with three-dimensional architectures have been reported.

For example, the tricoordinate dca$^-$ and tcm$^-$ anions form rutile-like structures M(tcm)$_2$ and M(dca)$_2$ (M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II));[4–5,7] some of them show long-range magnetic ordering, hard magnetic behaviour or spin-canted antiferromagnetism.[4–5]

Similarly, two other types of polynitrile, both involving six cyano groups, have also been used.[8–9] They led us to original three-dimensional compounds: [Ag(hcazpd)] with an intriguing structure generated from two different silver cations, one of them with unusual square-planar geometry,[8] and [M(tcpd)(H$_2$O)$_2$] (M = Mn(II), Fe(II), Co(II), Ni(II) and Cu(II)) generated by eclipsed chains which are laterally connected by equivalent eclipsed chains running orthogonally.[9] In addition to these binary compounds, mixed-ligand dca$^-$ and tcm$^-$ compounds



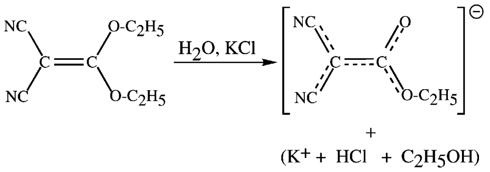
Scheme 1

with neutral bridging co-ligands such as pyrazine,[10] tetramethylpyrazine,[11] 1,2-bis(4-pyridyl)ethene,[11] hexamethylenetetramine,[12] 2,2′-bipyrimidine,[13] 2-aminopyrimidine,[14] pyrimidine[15] and 4,4′-bipyridine[11,16] have also been reported. In such context, our aim is to examine the ability of such polynitrile ligands to generate one-, two- and three-dimensional polymeric networks. This can contribute to our understanding of the binding modes of the tcnx (x = e or q) organic radicals in the binary molecular systems "metal/tcnx" (Scheme 1) that present unusual physical properties but for which the structural data are scarce.[1–2,17] Herein, we report the syntheses, structural characterisation and magnetic properties of new polymeric compounds of formulae $[\mathrm{M(dcne)_2(H_2O)_2}]$ (M = $\mathrm{Mn^{II}}$, **1**; $\mathrm{Fe^{II}}$, **2**; $\mathrm{Co^{II}}$, **3**; $\mathrm{Ni^{II}}$, **4** and $\mathrm{Zn^{II}}$, **5**) and $[\mathrm{Cu(dcne)_2(H_2O)}]$ (**6**) containing the bridging 2,2-dicyano-1-ethoxyethenolate anion (dcne$^-$ = $[\mathrm{(CN)_2CC(O)OEt}]^-$). Related studies of Mn and Cu derivatives of the 2,2-dicyano-1-methoxyethenolate anion ($[\mathrm{(CN)_2CC(O)OMe}]^-$) have been very recently reported.[18]

Results and discussion

Synthesis and general characterisation

The potassium 2,2-dicyano-1-ethoxyethenolate (Kdcne) was smoothly prepared by hydrolysis of the 1,1-diethoxy-2,2-dicyanoethylene; the initial pH value of 6.0 of the aqueous solution decreased to 1.0 after boiling the solution for a few minutes, consistent with the reaction shown in Scheme 2. This salt can be also prepared according to the method previously described by Middleton but gives only a low yield (≈30%).[19]



Scheme 2

Treatment of a saturated solution of K(dcne) with a saturated aqueous solution of the corresponding metal salt (either hydrated $\mathrm{MCl_2}$ or $\mathrm{MSO_4}$) in a dcne$^-$/M(II) ratio of 2 gave, after slow evaporation, the new compounds $[\mathrm{M(dcne)_2(H_2O)_2}]$ (M = $\mathrm{Mn^{II}}$, **1**; $\mathrm{Fe^{II}}$, **2**; $\mathrm{Co^{II}}$, **3**; $\mathrm{Ni^{II}}$, **4** and $\mathrm{Zn^{II}}$, **5**) and $[\mathrm{Cu(dcne)_2(H_2O)}]$ (**6**). All compounds can also be prepared in the same way as the potassium salt by direct reaction in aqueous solution of 1,1-diethoxy-2,2-dicyanoethylene with the corresponding metal salt. The IR spectra of all compounds [**1**–**6**, K(dcne) and $[\mathrm{Et_4N}]$(dcne)] show similar patterns with two strong absorption bands, in the 2180–2260 cm^{-1} region, assigned to ν_{CN}. Compared to the corresponding potassium and tetraethylammonium salts containing the non-coordinated dcne$^-$ moiety, the ν_{CN} bands observed in spectra of **1**–**6** are slightly shifted to higher wavenumbers (2160–2210 cm^{-1} region for K(dcne) and $[\mathrm{Et_4N}]$(dcne); 2200–2260 cm^{-1} region for **1**–**6**). This difference is due to the coordination of the organic ligand through its nitrile groups in **1**–**6**.[20] Broad features centred near 3400 cm^{-1} (ν_s and ν_{as}, OH) are indicative of the presence of water molecules but do not allow distinction between free and coordinated water molecules.

X-Ray crystal structures

Structures of $[\mathrm{Co(dcne)_2(H_2O)_2}]$ (3) and $[\mathrm{Zn(dcne)_2(H_2O)_2}]$ (5). Since preliminary studies indicated that compounds **1** to **5** were isostructural, single crystal structure determinations were only performed on compounds **3** and **5**. These compounds have a structure generated by a metal ion on a special position (0, *y*, 1/4), one organic ligand and a water molecule both located on general positions. Each metal ion is linked to four nitrogen atoms from four different organic ligands and to two symmetrically equivalent water molecules in *cis*-configuration. The coordination sphere of the metal atom can be described as a $\mathrm{MN_4O_2}$ pseudo-octahedron formed by a $\mathrm{MN_2O_2}$ plane arising from two nitrogen atoms (N1) and two water molecules (O1), with two nitrogen atoms (N2) in axial positions (Fig. 1b). The most important distortions of this polyhedron concern its equatorial angles (O1–M–O1: 81.07(6) and 80.97(7)°; N1–M–N1: 96.98(7) and 96.31(8)°, and O1–M–N1: 170.68(6) and 171.09(7)° for **3** and **5**, respectively) since the six bond lengths are almost equivalent (ranging from 2.066(1) to 2.120(1) Å in **3** and from 2.086(2) to 2.139(2) Å in **5**). The structure involves 12-membered $(\mathrm{M(NC{-}C{-}NC)_2M})$ dimetallacycles since two bridging dcne ligands connect two M(II) cations (Fig. 1a). These rings are almost planar, with a larger deviation from the corresponding mean plane of 0.02 Å in compound **3** and of 0.03 Å in compound **5**. Adjacent dimetallacycles are almost orthogonal with dihedral angles of 82.3° in **3** and of 82.2° in **5**. These rings share metal cations to give a chain of dimetallacycles running along the [101] direction (Fig. 1a). The intrachain M ··· M distances (7.4270(2) and 7.4628(2) Å for **3** and **5**, respectively) are longer than the inter-chain ones: 6.0430(4) and 6.0907(3) Å for **3** and **5**, respectively (see Fig. 1a). There are two types of hydrogen bonds between the coordinated water molecules (O1) and the terminal oxygen atom of the organic ligand (O2) joining parallel chains to give a 3D infinite lattice (Fig. 2). These hydrogen bonds present O1–O2 distances of 2.781(2) and 2.806(3) Å for **3** (2.818(3) and 2.808(2) Å for **5**) with O1–H ··· O2 angles of 172(1) and 173(2)° for **3** (172(2) and 173(2)° for **5**).

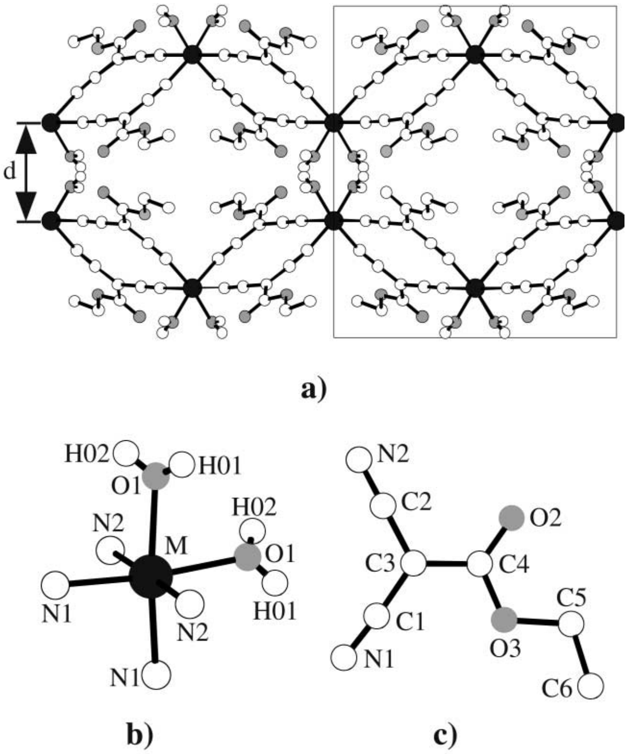


Fig. 1 a) Projection of **3** in the *ab* plane showing the monodimensional structure (M ··· M inter-chain distances: *d* = 6.0430(5) Å for **3** and *d* = 6.0907(3) Å for **5**); b) Metal environment in compound **3**; c) Structure of the dcne anion with the atom labelling scheme.

Structure of $[\mathrm{Cu(dcne)_2(H_2O)}]$ (6). The asymmetric unit of **6** contains a Cu(II) cation and a water molecule, both on special positions (0, *y*,1/4), and a dcne anionic ligand on a general position. As in **3** and **5**, each organic ligand acts in a bridging mode with its two nitrogen atoms N1 and N2 bound to two different copper cations (Fig. 3a). Each cation has a $\mathrm{CuN_4O}$

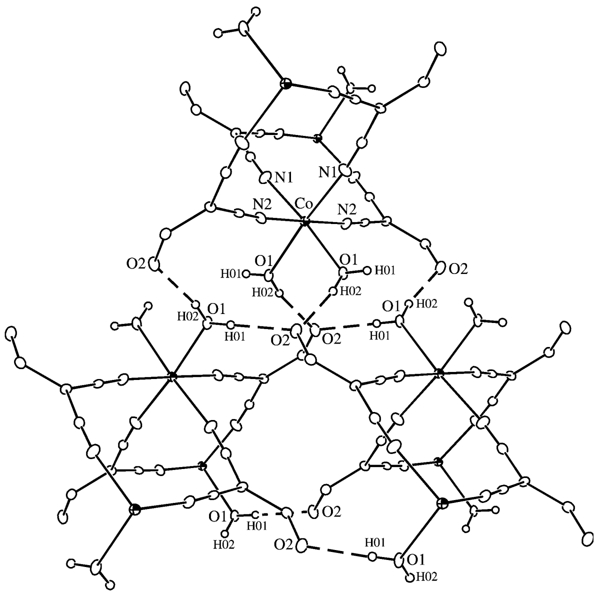


Fig. 2 ORTEP[30] perspective view of three adjacent chains along the [101] direction showing hydrogen bonds in **3**. The ethoxy groups, O(C_2H_5), are omitted for clarity.

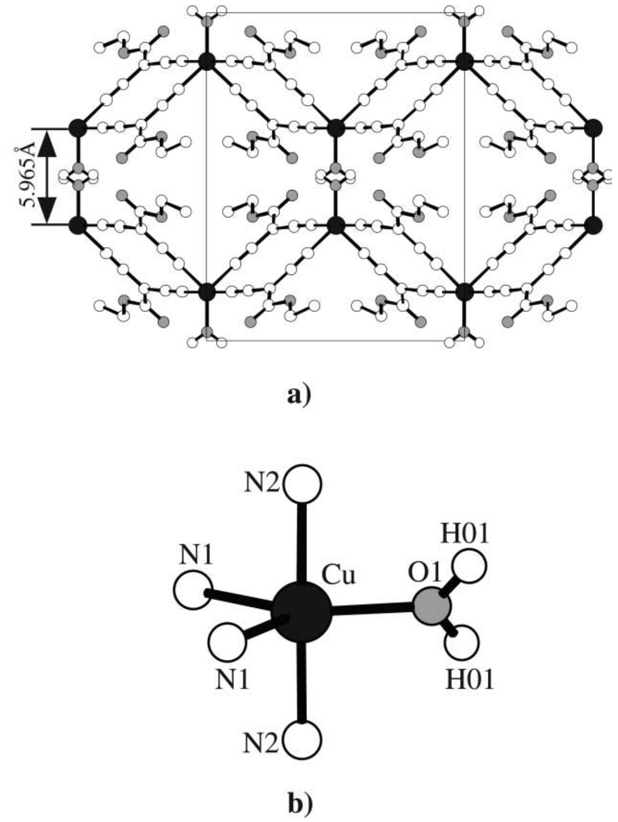


Fig. 3 a) Projection of **6** in the *ab* plane showing the monodimensional structure; b) Cu(II) environment in compound **6**.

Table 1 Selected bond lengths (Å) in compounds **3**, **5** and **6**

	3	5	6
M–O1	2.066(1)	2.086(2)	1.932(3)
M–N1	2.108(2)	2.139(2)	2.108(2)
M–N2	2.120(1)	2.139(2)	1.965(2)
O2–C4	1.225(3)	1.220(3)	1.222(3)
O3–C4	1.333(2)	1.329(2)	1.342(3)
O3–C5	1.457(3)	1.451(4)	1.451(3)
N1–C1	1.149(3)	1.148(2)	1.146(3)
N2–C2	1.142(2)	1.143(3)	1.143(3)
C1–C3	1.403(3)	1.409(3)	1.410(3)
C2–C3	1.411(2)	1.396(2)	1.400(3)
C3–C4	1.436(3)	1.437(3)	1.436(4)
C5–C6	1.435(3)	1.406(4)	1.487(3)

Table 2 Selected bond angles (°) in compounds **3**, **5** and **6**

	3	5	6
O1–M–O1	81.07(6)	80.97(7)	
O1–M–N1	91.18(7)	91.54(7)	129.80(6)
O1–M–N1	170.68(6)	171.09(7)	
O1–M–N2	91.51(6)	91.47(6)	89.65(7)
O1–M–N2	89.29(6)	89.63(6)	
N1–M–N1	96.98(7)	96.31(8)	100.39(9)
N1–M–N2	85.72(7)	85.71(7)	87.29(9)
N1–M–N2	93.59(7)	93.32(7)	93.15(9)
N2–M–N2	178.96(6)	178.55(7)	179.3(1)
C1–C3–C2	118.3(2)	118.3(2)	116.8(2)
C1–C3–C4	123.8(2)	123.3(2)	123.5(2)
C2–C3–C4	117.9(2)	118.3(2)	119.7(2)
O2–C4–O3	123.4(2)	123.1(2)	122.5(2)
O2–C4–C3	123.5(2)	123.5(2)	125.3(2)
O3–C4–C3	113.1(2)	113.4(2)	112.3(2)

trigonal bipyramid environment with four nitrogen atoms (two N1 and two N2) from four different organic ligands and one oxygen atom from a water molecule (Fig. 3b). This polyhedron, in which the bond lengths range from 1.932(3) to 2.108(2) Å, has a perfectly planar CuN_2O equatorial plane; examination of the crystallographic data depicted in Tables 1 and 2 shows that the most important distortion arises mainly from the equatorial angles (N1–Cu–N1 100.39(9)° and N1–Cu–O1 129.80(6)°). The molecular arrangement can be described as a chain generated by a planar dimetallacycle (the larger deviation from the mean plane is 0.06 Å) essentially equivalent to that described for compounds **3** and **5** and also running along the [101] direction (Fig. 3a). As in compounds **3** and **5**, adjacent dimetallacycles are almost orthogonal with a dihedral angle of 82.9°. The intra-chain Cu ··· Cu distance (7.2299(3) Å) is also longer than the inter-chain one (5.9648(5) Å) (see Fig. 3a) but slightly shorter than that reported for similar dimetallacycles in the 3D structure of [Cu(tcpd)(H_2O)$_2$] (7.434 Å).[9] As in **3** and **5**, an examination of the inter-chain distances reveals the presence of hydrogen bonds between the hydrogen atom of the coordinated water molecule (O1) and the terminal oxygen of the dcne ligand (O2). These hydrogen bonds occur between adjacent chains and present a O1–O2 distance of 2.705(2) Å with a O1–H ··· O2 angle of 173.9(1)°, giving rise to a 3D structure (Fig. 4).

In summary, the two extended molecular structures, that of **1**–**5** and that of **6**, are very similar, the main difference lying in the coordination polyhedron of the metal cations. In compound **6**, each Cu(II) cation resides in a distorted trigonal bipyramid environment, while in compounds **1**–**5**, the metal cations have a pseudo-octahedral geometry arising from one supplementary coordinated water molecule (Figs. 1b and 3b).

Structure of the dcne anion. Examination of bond lengths and bond angles clearly shows that the crystallographic parameters of the dcne ligand are not significantly different in compounds **3**, **5** and **6** (Tables 1 and 2 and Fig. 1c). Apart from the terminal ethyl group, the organic ligand is essentially planar within a maximum deviation of 0.07 Å from the corresponding mean plane. This is in agreement with an sp^2 hybridisation of the two central carbon atoms (C3 and C4), also shown by the bond angles around these atoms in each compound (sums of bond angles around C3: 360.0° in **3** and **6**, and 359.9° in **5**; sums of bond angles around C4: 360.0° in **3** and **5**, and 360.1° in **6**), associated with an sp hybridisation of the carbon atoms of the cyano groups. Crystallographic data depicted in Tables 1 and 2 for these compounds clearly show that the bonding in the dcne anion cannot be only explained by a simple Lewis structure

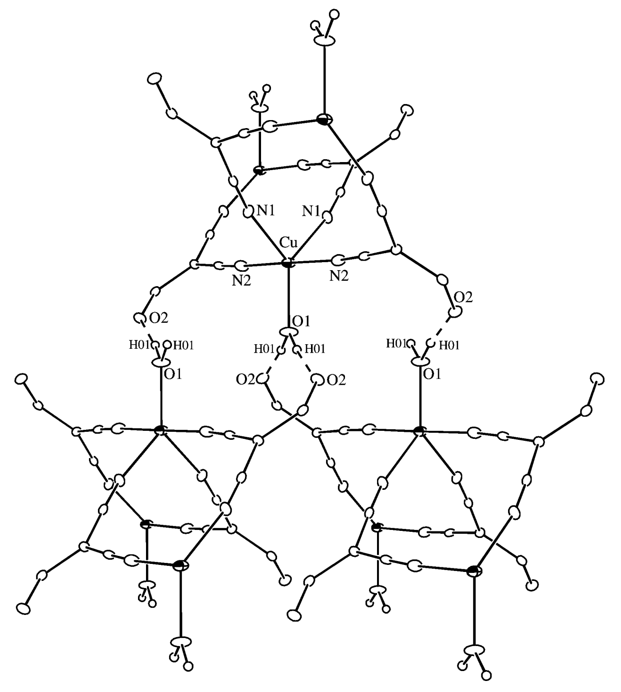
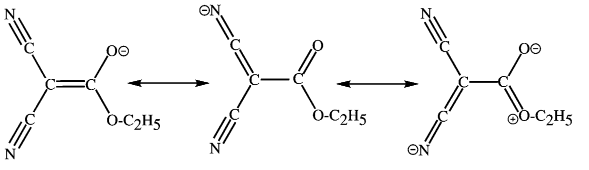


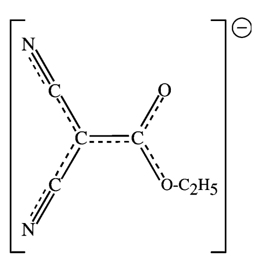
Fig. 4 ORTEP perspective view of three adjacent chains along the [101] direction showing hydrogen bonds in **6**. The ethoxy groups, $O(C_2H_5)$, are omitted for clarity.

since this unit contains a conjugated system which is highly delocalized. The delocalization is clearly shown by (i) a rather short terminal C4–O2 bond (average value *ca.* 1.222(3) Å) which strongly deviates from a normal C–O single bond (1.50 Å), (ii) a central C3–C4 bond (average value 1.436 Å) longer than a normal C=C double bond (1.34 Å), (iii) two C–CN bonds (average value 1.405 Å) and a C4–O3 bond (average value. 1.335 Å) which all present some character of multiplicity. These observations indicate that the organic anion can be considered as a resonance hybrid of different canonical structures (Scheme 3).



Scheme 3

These three forms, and the symmetrical ones not shown on the scheme, give rise to the mean electronic structure of Scheme 4 which agrees well with the planarity of the $[(NC)_2$-



Scheme 4

CC(O)O] group and with the structural data (Tables 1 and 2). Thus, it is clear that in this ligand the negative charge is not mainly located on the terminal oxygen atom and therefore it is not surprising that this atom does not enter into the coordination sphere of the metal.

Magnetic properties

The magnetic properties of all the samples (except the Zn derivative, which is diamagnetic) are displayed in Fig. 5 as the thermal dependence of the $\chi_m T$ product, where χ_m is the magnetic susceptibility per mol of metal ion. The room temperature $\chi_m T$ values (4.4, 3.5, 3.0, 1.2 and 0.45 emu K mol^{-1} for the Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} derivatives, respectively) are in good agreement with the observed values for the corresponding metal ions in dicyanamide analogues.[11,13,16] When cooling down the $\chi_m T$ products for **1**, **2**, **4** and **6** remain constant down to approx. 50 K where a decrease initiates. In the cobalt derivative (**3**), the decrease in the $\chi_m T$ product starts at higher temperatures due to the orbital contribution present in this ion. At 2 K the $\chi_m T$ values are 2.25, 1.85, 1.90, 0.85, and 0.39 emu K mol^{-1} for **1**–**4** and **6**, respectively. This decrease in the $\chi_m T$ product must be due to very weak antiferromagnetic coupling between metal ions in the Mn^{II}, Fe^{II}, Ni^{II} and Cu^{II} derivatives. In the zinc derivative (**5**), we observe the expected diamagnetic behaviour for a d^{10} ion. No susceptibility maxima are observed in the studied temperature range (2–300 K). The weak coupling can be understood from the long M ··· M distance imposed by the two –NC–C–CN– bridges connecting the metal centres. From the structural data, that indicate the presence of regular chains in these compounds, we have fitted their magnetic susceptibilities to a classical regular chain model with the Hamiltonian:[21] $H = -J\Sigma S_i S_{i+1}$, where $S_i = S_{i+1} = 5/2$ (Mn), 2 (Fe), 1 (Ni) or 1/2 (Cu). The analytical expression is:[22]

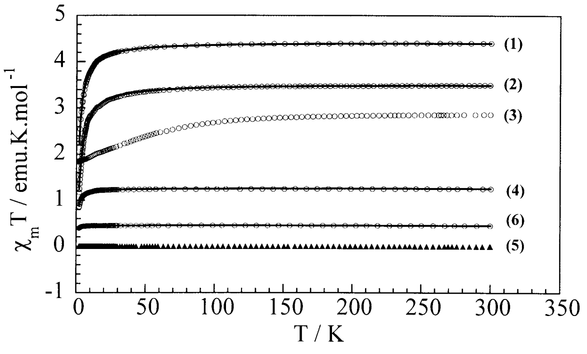


Fig. 5 Thermal variations of the magnetic susceptibility in the forms $\chi_m T$ *vs.* T for **1**–**6**. Solid lines represent the best fit to the regular spin chain model (see text and Table 3).

$$\chi_m = \frac{2N\beta^2 g^2}{kT}\left(\frac{1+u}{1-u}\right), \text{ where } u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$$

This expression gives a very satisfactory agreement with the experimental data in the whole temperature range with the sets of parameters displayed in Table 3 (solid lines in Fig. 5). The J values found for the Mn and Cu derivatives (−0.249 and −0.043 cm^{-1}, respectively) are very similar to those recently reported for the Mn and Cu complexes of the methyl ester of the dicyano-acetic acid (−0.21 and −0.032 cm^{-1}, respectively) that present the same type of bridge between the metal centres.[18]

Table 3 Magnetic parameters for the series of compounds $M(dcne)_2(H_2O)_2$ (M = Mn (**1**), Fe (**2**), Ni (**4**)) and for $M(dcne)_2(H_2O)$ (**6**)

M^{II}	S	g	J/k (cm^{-1})	θ/K
Mn	5/2	2.0103(3)	−0.249(1)	−2.10(9)
Fe	2	2.1666(8)	−0.387(2)	−0.38(4)
Ni	1	2.2483(7)	−0.125(1)	−0.83(2)
Cu	1/2	2.1985(3)	−0.043(1)	−0.34(1)

Note that we have not considered the possible inter-chain magnetic interactions nor the zero field splitting of the metal ions. As mentioned in the Experimental section, an important point to underline is the need to avoid the torquing of the Fe(II) and Co(II) samples by pressing them in pellets.

A final proof of the antiferromagnetic nature of the magnetic interaction comes from the isothermal magnetisation data (Fig. 6) that show in all cases a behaviour close to that expected for isolated magnetic centres (Brillouin function) but with lower values. This fact can be related to the non-negligible population of the $S = 0$ ground state at 2 K and confirms the presence of antiferromagnetic exchange interactions in all compounds. A Brillouin function where the temperature has been substituted by a $T - \theta$ term, to account for these antiferromagnetic interactions has been used to fit the magnetisation data with satisfactory agreement in all the cases and with the set of parameters displayed in Table 3 (solid lines in Fig. 6).

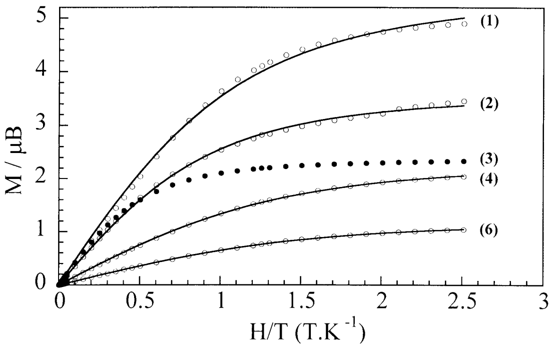


Fig. 6 Isothermal magnetisation at 2 K for **1**–**4** and **6**. Solid lines represent the best fit to the modified Brillouin function (see text).

Concluding remarks

This study involves the design of some new monodimensional polynitrile-transition metal compounds and shows that the 2,2-dicyano-1-ethoxyethenolate $[(CN)_2CC(O)OEt]^-$ ligand can present a bridging coordination mode similar to that observed by the μ-dicyanamide ligand in many derivatives.[4,10–16,23] Structural data indicate that this planar and highly conjugated ligand leads to monodimensional chains of 12-membered dimetallacycles. The low dimensionality of these compounds is essentially caused by (i) the presence of coordinated water molecules which reduce the number of "M–dcne" coordinated sites around the metal cations, and (ii) by the *cis*-arrangement of these water molecules in **1**–**5**. In an effort to increase the dimensionality and the cooperativity between the metal ions as observed in the dicyanamide binary systems having the rutile-like structure, we are turning to syntheses in non-aqueous media, using organic solvents and the tetraethylammonium salt of the polynitrile instead of the potassium salt. Extension of this study to other conjugated polynitriles (cyano- or azacyano-carbanions) such as the tcpd^{2-} anion[9] or the $[C_{10}N_8]^{\bullet-}$ radical anion[24] is in progress in order to obtain a more unified view in the bonding/electronic structure relationship in these highly conjugated systems. This might lead to a rationalisation of their properties of interest, electronic delocalization within the ligand and magnetism.

Experimental

Materials

The reagents tetracyanoethylene, urea, KCl, $MnCl_2{\cdot}4H_2O$, $FeSO_4{\cdot}7H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$ and $ZnSO_4{\cdot}7H_2O$ were purchased from commercial sources and used as received. All reactions were performed under aerobic conditions.

Physical measurements

Infrared spectra were recorded in the range 4000–200 cm^{-1} as KBr pellets on a FT–IR NEXUS NICOLET spectrometer. NMR spectra were carried out on a Bruker AMX 400 MHz instrument. Elemental analyses were obtained from the Service de microanalyses, CNRS, Gif sur Yvette, France. The magnetic studies were carried out on powder samples enclosed in medical caps. The magnetic susceptibility measurements were performed at 0.1 T, in the temperature range 2–300 K with a SQUID magnetometer MPMS–XL-5 from Quantum Design. In the Co(II) and Fe(II) compounds the initial magnetic measurements on randomly oriented polycrystalline samples showed an increase in the $\chi_m T$ product at low temperature. This increase was observed at higher temperature in the iron compound. These effects, which are due to the anisotropy of the susceptibility of the samples, have already been observed in Fe(II) and Mn(III) compounds.[26] In order to remove these effects, the measurements were performed on pressed pellets to prevent crystallite torquing. In these conditions no increase was observed for the $\chi_m T$ product at low temperatures, as expected for magnetically isolated or very weakly coupled systems. The molar susceptibility was corrected from the sample holder and diamagnetic contributions of all atoms (Pascal's tables).

Synthesis

1,1-Diethoxy-2,2-dicyanoethylene. This acetal was first prepared following the procedure previously reported by Middleton[19] but this procedure in our hands only gave a bad yield (5–10%). Since during this synthesis it has been observed that the time of heating is a crucial parameter, several syntheses were then performed with different heating times. The best yield (58%) was obtained as follows: A warm ethanolic solution (20 mL) containing 3.2 g (25 mmol) of tetracyanoethylene and 1.5 g (25 mmol) of urea was heated with continuous stirring at 70 °C over four minutes. The resulting solution was then immediately poured into 150 mL of cold water and kept in a refrigerator for a day to give white needles of the acetal which were separated by filtration. The solidified brown oil which was also obtained at this time was dissolved in diethyl ether; after filtration to remove black impurities and slow evaporation of the resulting filtrate, a second crop of acetal was collected on a filter. Anal. calc. for $C_8H_{10}N_2O_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.35; H, 6.10; N, 17.11%. IR data (ν/cm^{-1}) on KBr pellets: 3435br, 2219m, 2209m, 1551s, 1478w, 1463w, 1442m, 1387m, 1358w, 1332m, 1229w, 1214w, 1175m, 1147w, 1104w, 1012w, 998w, 854w, 711w, 696w, 596w, 554w, 454w. NMR ^{13}C data in $CDCl_3$ (δ/ppm): 175.3 ($C(OEt)_2$), 113.4 (CN), 69.7 ($O{-}CH_2{-}CH_3$), 44.1 ($C(CN)_2$), 14.6 ($-O{-}CH_2{-}CH_3$).

Potassium 2,2-dicyano-1-ethoxyethenolate. KCl (1.79 g, 24 mmol) was added to a hot aqueous solution of 1,1-diethoxy-2,2-dicyanoethylene (2.00 g, 12 mmol). The solution was stirred and heated until the solid dissolved. Slow evaporation of the resulting solution at room temperature gave crystals of potassium 2,2-dicyano-1-ethoxyethenolate as white needles (95% yield). Anal. calc. for $C_6H_5N_2O_2K$: C, 40.90; H, 2.86; N, 15.90; K, 22.19. Found: C, 40.21; H, 2.81; N, 15.68; K, 22.29%. IR data (ν/cm^{-1}) on KBr pellets: 3452br, 2209s, 2181s, 1642s, 1482w, 1404w, 1375m, 1321s, 1278w, 1145m, 1105w, 1024w, 755w, 553w. In order to perform the NMR measurement in an organic solvent, the corresponding tetraethylammonium salt was prepared by metathesis of the potassium salt with $[Et_4N]Cl$ in a minimum amount of water. NMR ^{13}C data in $CDCl_3$ (δ/ppm) for $[Et_4N][dcne]$: 171.1 ($CO(OEt)$), 123.4 (CN), 59.0 ($O{-}CH_2{-}CH_3$), 52.6 ($^+N(CH_2CH_3)_4$), 31.8 ($C(CN)_2$), 14.9 ($-O{-}CH_2{-}CH_3$), 7.6 ($^+N(CH_2CH_3)_4$). These data are in agreement with those previously reported for this anion.[25]

Table 4 Crystal data for compounds **1**–**6**

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_{12}H_{14}N_4O_6Mn$	$C_{12}H_{14}N_4O_6Fe$	$C_{12}H_{14}N_4O_6Co$	$C_{12}H_{14}N_4O_6Ni$	$C_{12}H_{14}N_4O_6Zn$	$C_{12}H_{12}N_4O_5Cu$
Formula weight[a]	365.21	366.12	369.20	368.98	375.64	355.79
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*	*C*2/*c*
a/Å	14.334(4)	14.227(4)	14.0331(8)	13.939	14.1182(4)	12.8978(6)
b/Å	15.721(5)	15.570(6)	15.415(1)	15.413	15.5441(4)	15.8015(9)
c/Å	7.973(3)	7.993(4)	7.9596(5)	7.929	7.9715(2)	7.3402(5)
β/°	110.47(1)	110.53(1)	110.870(5)	111.29	110.874(2)	105.963(5)
V/Å^3	1683	1658	1608.8	1687	1634.6	1438.3
Z[a]	4	4	4	4	4	4
D_c/g cm^{-3}	1.441	1.441	1.524	1.544	1.526	1.643
μ/cm^{-1}			10.96		15.70	15.48
Reflections measured			3284		4589	2838
Reflections unique/R_{int}			1859/0.027		2374/0.013	1644/0.033
Reflections with $I > n\sigma(I)/N_v$			1538 ($n = 2$)/113		1672 ($n = 4$)/113	1158 ($n = 2$)/101
$R(F_o)$[b]/$R_w(F_o)$[c]			0.035/0.040		0.032/0.046	0.036/0.040
G.O.F[d]			1.293		1.232	1.080
$\Delta\rho_{max, min}$/e Å^{-3}			0.252, −0.329		0.262, −0.277	0.146, −0.266

[a] The asymmetric unit contains 0.5 of the chemical formula. [b] $R = \Sigma|F_o - F_c|/F_o$. [c] $Rw = [\Sigma w(|F_o| - |F_c|)^2/w(F_o)^2]^{1/2}$. [d] $G.O.F = [(\Sigma w|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{1/2}$.

Compounds 1–6. These six compounds were prepared in the same way by treating saturated aqueous solutions of the corresponding metal chloride or metal sulfate with saturated solutions of potassium 2,2-dicyano-1-ethoxyethenolate in a M/dcne ratio of 1/2. The samples were stirred without heating for ten minutes and left to stand. Slow evaporation of the resulting solutions at room temperature gave prismatic crystals for compounds **1**–**3** and **5**–**6** and only a powder for **4**. All compounds were satisfactorily analysed for C, H and N. Anal. calc. for $C_{12}H_{14}N_4O_6M$: (**1**): C, 39.5; H, 3.9; N, 15.3. Found: C, 39.6; H, 3.9; N, 15.5%. (**2**): C, 39.4; H, 3.9; N, 15.3. Found: C, 39.3; H, 4.0; N, 15.4%. (**3**): C, 39.0; H, 3.8; N, 15.2. Found: C, 39.0; H, 3.9; N, 15.0%. (**4**): C, 39.1; H, 3.8; N, 15.2. Found: C, 39.1; H, 3.8; N, 15.4%. (**5**): C, 38.4; H, 3.8; N, 14.9. Found: C, 38.3; H, 3.9; N, 15.0%. Anal. calc. for $C_{12}H_{12}N_4O_5Cu$ (**6**): C, 40.5; H, 3.4; N, 15.8. Found: C, 40.3; H,3.5; N, 16.0%. IR data (ν/cm^{-1}): for **1**: 3406br, 2236s, 2201s, 1647m, 1617s, 1480w, 1413w, 1378m, 1331s, 1153m, 1111w, 1019w, 760w, 558w; for **2**: 3397br, 2236s, 2201s, 1643m, 1616s, 1480w, 1413w, 1378m, 1330s, 1152m, 1111w, 1019w, 759w, 559w; for **3**: 3398br, 2242s, 2206s, 1616s, 1480w, 1413w, 1378m, 1330s, 1152m, 1110w, 1020w, 760w, 558w; for **4**: 3403br, 2249s, 2215s, 1615s, 1480w, 1413w, 1378m, 1331s, 1151m, 1108w, 1021w, 760w, 556w; for **5**: 3408br, 2243s, 2209s, 1645m, 1616s, 1481w, 1413w, 1377m, 1328s, 1148m, 1109w, 1020w, 759w, 557w; for **6**: 3341br, 2254s, 2206s, 1653s, 1478w, 1404w, 1374m, 1325s, 1145m, 1107w, 1022w, 754w, 556w.

X-Ray crystallography

Cell parameters of all compounds (**1**–**6**) were obtained from single crystal diffraction for **1**–**3** and **5**–**6** and from powder patterns for **4** (Table 4).[27] Preliminary studies showed that compounds **1**–**5** were isostructural and therefore crystal data collection was only performed for **3** and **5**. Crystallographic data of compounds **3**, **5** and **6** were collected (T = 173 K for **3** and **6** and T = 290 K for **5**) on a Nonius KappaCCD diffractometer. The three structures were solved by direct methods and successive Fourier difference syntheses, and were refined on F by weighted anisotropic full-matrix least-squares methods.[28] The dcne hydrogen atoms were calculated [d(C–H) = 0.95 Å]; the thermal parameters were taken as $U_{iso} = 1.3\ U_{eq}(C)$ and therefore included as isotropic fixed contributors to F_c in the three structures. Those of the water molecules were located by difference Fourier maps and refined isotropically, except those of compound **6** which were not refined. Scattering factors and corrections for anomalous dispersion were taken from the *International Tables for X-Ray Crystallography*.[29] All calculations were performed on an Alphastation 255 4/233 computer. Pertinent crystal data, selected bond distances and selected bond angles of **3**, **5** and **6** are listed in Tables 4, 1 and 2 respectively.

CCDC reference numbers 169972–169974.

See http://www.rsc.org/suppdata/dt/b1/b107944c/ for crystallographic data in CIF or other electronic format.

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27 Compounds **1**–**5** display similar powder X-ray diffraction patterns; indexing that of Ni(dcne)$_2$(H$_2$O)$_2$ (**4**) gave the *I*-centred monoclinic crystal system with $a = 13.301$, $b = 15.413$, $c = 7.929$ Å, $\beta = 102.45°$. Transformation to the *C*-centred lattice gave the cell parameters depicted in Table 4.

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