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Review

Chemistry and magnetism of cyanido-bridged d–f assemblies

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Contents

Abstract

Design and synthesis of cyanido-bridged d–f molecular assemblies, often accessible via self-assembly of anionic building-block $[M(CN)_6]^{3-}$ and lanthanide ions in the presence of blocking ligands, is of significant utility in the preparation of molecule-based magnets. The ability of the cyanido ligand to link various metal ions leads to a wide diversity of structural architectures ranging from discrete polynuclear complexes to fascinating three-dimensional networks. In this review, examples of cyanido-bridged d–f polynuclear complexes are discussed in terms of their structures, and their magnetic properties. It is shown that the efforts to synthesize d–f cyanido-bridged assemblies have lead to a great variety of supramolecular architectures created by the interplay of coordinative, hydrogen bonding, and π–π stacking interactions. Furthermore, the magnetic properties of these assemblies will be discussed in terms of the magnetic exchange coupling between lanthanide(III) and transition metal ions.

Keywords: Cyanido ligand; d–f complexes; Spin-coupling mechanism

1. Introduction

Driven by the progressive decrease of component size in conventional electronics, chemists in recent years have begun to create some of the basic building-blocks needed for the self-assembly of nanoscale molecular devices including metals, semiconductors, and molecule-based magnets [1–7]. In this respect, cyanido-metallate complexes have been widely studied in many fields, mainly because of their rich and interesting structures, magnetic and catalytic properties [8–15]. The most popular approach to the synthesis of cyanido-bridged magnetic materials has been to use an anionic building-block $[M(CN)_6]^{n-}$ (M = Cr(III), Mn(III), Fe(II), Fe(III), Co(III)) in conjunction with transition metal aqua complexes, $[M'(H_2O)_x]^{m+}$ or cationic assembler units of the type $[M'(\text{ligand})_x]^{m+}$ (M′ = Mn(II), Mn(III), Co(II), Ni(II), Cu(II)). The ability of the cyanido group to link various metal ions lead to a wide diversity of structural architectures ranging from discrete polynuclear complexes to various three-dimensional networks [8–14]. In all cases, the

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Abbreviations: OAc, acetate; bet, betaine; bpy, 2,2′-dipyridyl; bpym, 2,2′-bipyrimidine; capro, caprolactam; dma, *N*,*N*-dimethylacetamide; dmf, *N*,*N*-dimethylformamide; dpdo, 2,2′-dipyridyl-*N*,*N*′-dioxide; gly, glycine; hp, 4-hydroxypyridine; phen, 1,10-phenanthroline; pyr, pyrrolidinone; H_2salpn, *N*,*N*′-propylenedi(3-methoxysalicylideneiminato); L_1, 4,4′-dipyridyl-*N*,*N*′-dioxide; L_2, 1,4,8,11-tetra-azacyclotradecane-2,3-dione

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cyanido group in addition to its structural function also provided an important exchange path mediating the interaction between electrons localized on paramagnetic centers. These features have allowed considerable control over the nature and magnitude of the local magnetic exchange interactions [16–24]. As for high-T_c materials, different vanadium–chromium cyanido complexes with T_c above room temperature have been reported by Verdaguer and co-workers ($T_c = 310$ K) [25], Miller and co-workers ($T_c = 372$ K) [26], and Girolami and co-workers ($T_c = 376$ K) [27]. It has also been shown that the magnetism can be controlled by electrochemical stimuli and optical stimuli in some of the Prussian blue analogues [28–34].

Recent advances in the design of cyanido-bridged molecular-based magnetic materials have led to the isolation of discrete as well as supramolecular polynuclear d–f complexes [15,35–46]. These d–f polymetallic assemblies open new perspectives for (i) the study of the magnetic interactions between transition- and lanthanide-metal ions through the cyanido bridge; (ii) the use of the optical properties of the lanthanide ion included in molecular magnetic media, and (iii) the design of new materials for heterogeneous catalysis. Besides, the introduction of paramagnetic lanthanide ions can lead to new and interesting properties of the magnetic materials because of the large and anisotropic magnetic moment of these metal ions. One convenient route toward d–f cyanido-bridged complexes is a methatesis reaction between a lanthanide(II, III) salt and a tetracyanidometallate salt (i.e. $[M(CN)_4]^{2-}$, M = Ni(II), Pd(II), Pt(II)) in highly polar solvents, thus forming one-dimensional, two-dimensional and three-dimensional arrays [15,47–57]. In particular, the three-dimensional arrays have been proven to be useful as heterogeneous catalysts precursors [56]. Two types of d–f cyanido-bridged bi- or trimetallic assemblies derived from $[M(CN)_6]^{n-}$ (M = Cr(III), Mn(III), Fe(III), Co(III)), namely Prussian blue-like phases and molecular species, have been obtained. The former, complexes of general composition $[LnM(CN)_6]\cdot xH_2O$ (M = Cr(III), Fe(III); $x = 4$ or 5) are three-dimensional cyanido-bridged network solids and their structure and magnetic properties have been reported [58–63]. Ferrimagnetic ordering was observed for $[LnCr(CN)_6]\cdot xH_2O$ (Ln = Nd(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III)) and $[TbCr(CN)_6]\cdot 4H_2O$ has the highest magnetic phase transition temperature ($T_c = 11.7$ K) [63]. The use of blocking organic ligands in order to reduce the three-dimensionality of these complexes results in various molecular architectures and this review is focused on these complexes and their magnetic properties.

2. Heterodimetallic d–f assemblies

2.1. Dinuclear cyanido-bridged complexes

After the report on the first dinuclear d–f cyanido-bridged complex in 1998, $[Sm(dmf)_4(H_2O)_4Fe(CN)_6]\cdot H_2O$ (dmf = *N*,*N*-dimethylformamide) [64], interest in heterodimetallic lanthanide-transition metal complexes with cyanido bridges and with various stages of hydration has been long-standing in a few groups and several d–f dinuclear complexes have been published: (i) $[Ln(dmf)_4(H_2O)_3M(CN)_6]\cdot H_2O$ [65–68] (Ln = La(III), Ce(III), Nd(III), Sm(III), Gd(III), Er(III), Yb(III); M = Fe(III), Co(III)); (ii) $[Ln(dmf)_4(H_2O)_3M(CN)_6]\cdot xH_2O$ with $1 \leq x \leq 2$ (Ln = Ce(III), Pr(III), Sm(III), Tm(III), Yb(III); M = Fe(III), Co(III)) [37]; (iii) $[Ln(pyr)_4(H_2O)_3Fe(CN)_6]\cdot xH_2O$ with $x = 1$ or 2 (Ln = Ce(III), Pr(III), Nd(III), Eu(III), Gd(III), Tb(III), Dy(III), Er(III); pyr = pyrrolidinone) [69]; (iv) $[Ho(dma)_3(H_2O)_3Fe(CN)_6]\cdot 3H_2O$, dma = *N*,*N*-dimethylacetamide [70], and (v) $[Gd(dpdo)_2(H_2O)_3Fe(CN)_6]\cdot 4H_2O$, dpdo = 2,2′-dipyridyl-*N*,*N*′-dioxide [40]. The preparation of these assemblies can be easily achieved by the reaction of the lanthanide(III) salts and $K_3[M(CN)_6]$ (M = Mn(III), Fe(III), Co(III)) in a 1:1 stoichiometry and in the presence of an organic ligand. Typically, polycrystalline materials are obtained by slow evaporation of the aqueous solutions at room temperature and in the dark. The IR spectra of these complexes show a group of narrow and strong bands between 2100 and 2200 cm^{-1} that correspond to the $\nu_{C\equiv N}$ stretching frequency. The shift of $\nu_{C\equiv N}$ to higher wavenumber as compared to that of $K_3[M(CN)_6]$ is consistent with the formation of cyanido bridge. The fact that there is more than one band indicates that the cyanido ligand has more than a single coordination mode. The $\nu_{C\equiv N}$ stretching frequency of the terminal cyanido ligand falls in the range 2000–2100 cm^{-1} whilst the range 2100–2200 cm^{-1} is characteristic for the cyanido ligand that acts as a bridge or/and the terminal cyanido ligand involved in hydrogen bonding interactions [71].

Crystallographic investigations have been reported for most of the above-mentioned complexes. The molecular structure consists of a cyanido-bridged array of $[Ln(ligand)_n(H_2O)_3]^{3+}$ ($n = 2$, 3 or 4) and $[M(CN)_6]^{3-}$ fragments forming heterodimetallic molecular entities linked by a cyanido-bridged ligand (Fig. 1). The lanthanide(III) ion is either eight-coordinated with a distorted dodecahedral or square anti-prism geometry [64] or nine-coordinated with the coordination polyhedron best described as tricapped trigonal prism [38,40,65,68,72]. The geometry of the $[M(CN)_6]^{3-}$ entity is approximately octahedral, with the Ln–NC–M linkage deviating from linearity due to steric

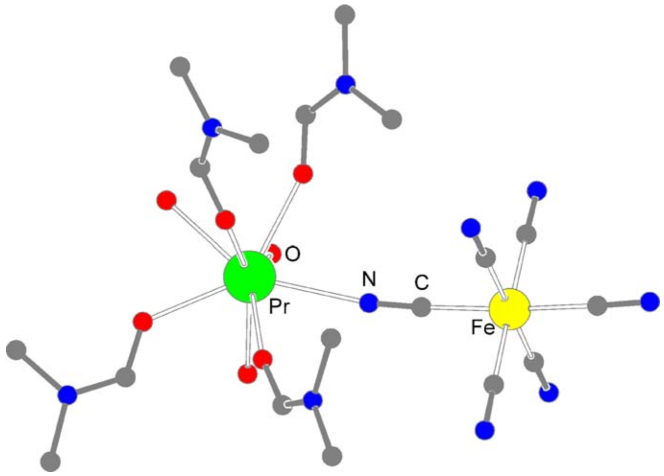

Fig. 1. Projection of the dinuclear unit of $[Pr(dmf)_4(H_2O)_3Fe(CN)_6]\cdot H_2O$ [37]. Lattice water molecules have been omitted for clarity.

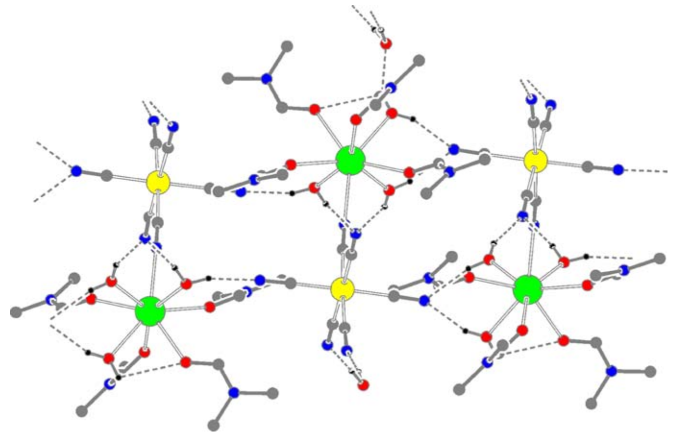

Fig. 2. View of the hydrogen bonding network of $[Pr(dmf)_4(H_2O)_3Fe(CN)_6]\cdot H_2O$ [37].

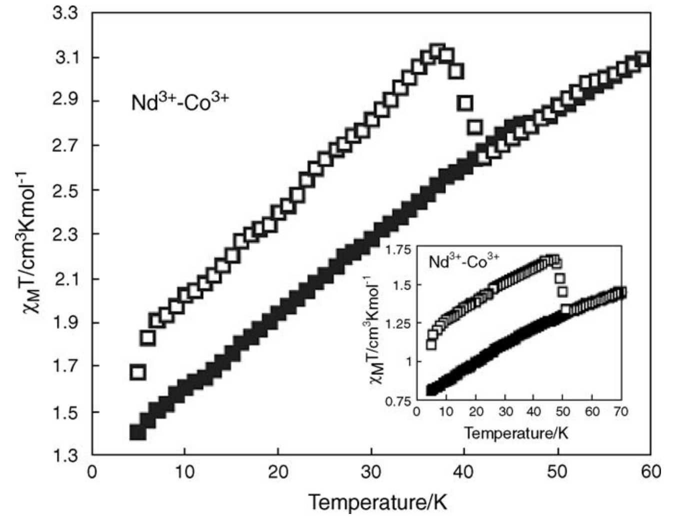

Fig. 3. Magnetic susceptibility (χ_MT) versus temperature (T) curves of $[Nd(dmf)_4(H_2O)_3M(CN)_6]\cdot H_2O$ (M = Fe, Co) at H = 5000 G before (■) and after (□) irradiation [72,73].

factors and crystal packing forces; the M–C≡N angle falls in the range 175.2–179.0°. The intramolecular distances between the two metals through the cyanido bridge is observed in the range 5.352–5.580 Å. Hydrogen bonding and van der Waals cohesive forces are paramount in the intermolecular network of the crystal lattices of these complexes, since the neutral dinuclear units are often linked by hydrogen bonds in a three-dimensional network (Fig. 2).

Three types of magnetic behaviour have been observed for the d–f dinuclear complexes presented above: negligible interactions, antiferromagnetic and ferromagnetic exchange intramolecular magnetic coupling interactions. In some cases, intermolecular interactions through hydrogen bonding have been observed at very low temperatures. In order to gain insights in the nature of the lanthanide-transition metal ion exchange magnetic coupling, Diaz and co-workers have compared the magnetic susceptibility data of isostructural Ln(III)–Fe(III) and Ln(III)–Co(III) complexes together with the magnetic properties of the La(III)–Fe(III) complex in order to take into account the anisotropy of the low-spin Fe(III) ion [37]. Thus, it has been found that the Ln(III)–Fe(III) exchange magnetic coupling is antiferromagnetic for the cases of Ln = Ce(III), Nd(III), Gd(III) and Dy(III), but ferromagnetic for the case of Ln = Tb(III), Tn(III), Ho(III) [37]. Negligible magnetic interactions have been observed Ln(III)–Fe(III), where Ln = Pr(III), Eu(III), Er(III), Sm(III), and Yb(III) [37]. Controversially, the temperature-dependent magnetic susceptibility measured at different magnetic fields has indicated a weak ferromagnetic interaction between the Gd(III) and Fe(III) ions in the complexes $[Gd(dpdo)_4(H_2O)_3Fe(CN)_6]\cdot 4H_2O$ ($J_{GdFe} = 0.4\ cm^{-1}$) and $[Gd(pyr)_4(H_2O)_3Fe(CN)_6]\cdot 2H_2O$ ($J_{GdFe} = 0.735\ cm^{-1}$) [40,69]. These differences have been attributed to the presence of hydrogen-bonding interactions present in the crystal lattice that can give important intermolecular interactions, thus hiding the Ln(III)–Fe(III) intramolecular interaction in the low-temperature range [37,40].

Einaga and co-workers [72–74] have reported that the magnetic properties of the complexes $[Nd(dmf)_4(H_2O)_3M(CN)_6]\cdot H_2O$ (M = Fe(III), Co(III)) can be influenced by external stimuli in a given temperature range. Upon UV light irradiation at 5 K, the magnetization of these complexes was slowly increased and gradually saturated after several hours. The curves χ_MT versus temperature show that the χ_MT values are enhanced (about 45% for Nd–Fe and 25% for Nd–Co) as compared to those before irradiation (Fig. 3) [72,73]. In both cases, the photo-excited state was stable for at least several hours at 5 K. Upon increasing the temperature to 50 K, the photo-induced magnetization disappears suggesting that the photo-excited state is relaxed to the ground state. This behaviour has been interpreted in terms of light-induced ligand-to-metal charge transfer transition in the case of the Nd(III)–Fe(III) complex whilst a charge transformation or/and or polarization from Nd(III) to diamagnetic Co(III) has been postulated for the Nd(III)–Co(III) complex [72,73].

2.2. *Trinuclear cyanido-bridged complexes*

Two kinds of d–f trinuclear cyanido-bridged complexes have been reported: (i) $[\{Gd(dma)_3(H_2O)_4\}_2Fe(CN)_6]\cdot 3H_2O$ [75] and (ii) $[Ln_2M(CN)_6(bpy)_4(H_2O)_8][M(CN)_6]\cdot 8H_2O$ (Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III); M = Fe(III), Co(III); bpy = 2,2′-dipyridyl) [76,77]. In general, the Ln_2M trinuclear complexes are obtained by stoichiometric reaction of $Ln(NO_3)_3\cdot nH_2O$ and $K_3[M(CN)_6]$ in aqueous solution and in the presence of the organic ligand, dma or bpy. In the complex $[\{Gd(dma)_3(H_2O)_4\}_2Fe(CN)_6]\cdot 3H_2O$, the $[Fe(CN)_6]^{3-}$ entity is connected to two gadolinium(III) ions via two bridging cyanido groups [70]. The two Gd(III) ions are each eight-coordinated, the coordination sites being occupied by seven oxygen atoms from three dma molecules and four H_2O molecules; the seven coordination site is occupied by one coordinating nitrogen atom from the bridging cyanido ligand. The three uncoordinated water molecules are involved in hydrogen-bonding interactions with the trinuclear entity as well as the counter ion $[M(CN)_6]^{3-}$, thus resulting in a extended network. The $[M(CN)_6]^{3-}$ unit adopts a distorted octahedral conformation with the bond angles Fe–C≡N ranging from 174.0°

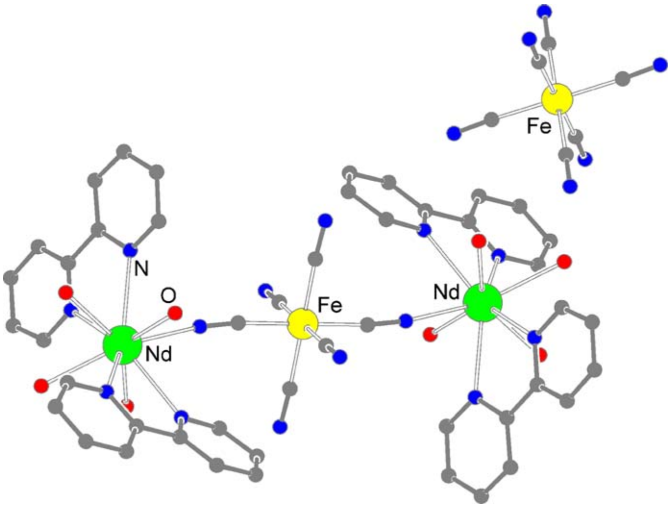

Fig. 4. View of the molecular structure of the complex $[Nd_2Fe(CN)_6(bpy)_4(H_2O)_8][Fe(CN)_6]\cdot8H_2O$. Lattice water molecules have been removed for clarity [76,77].

to 179.0°. The variable-temperature magnetic susceptibility studies for the complex $[[Gd(dma)_3(H_2O)_4\}_2Fe(CN)_6]\cdot3H_2O$ revealed an intramolecular antiferromagnetic interaction between the adjacent Gd(III) ($S=7/2$) and Fe(III) ($S=1/2$) ions through the cyanido bridge, with the Curie and Weiss constants being equal to $2.26\,cm^3\,K\,mol^{-1}$ and -44.3 K, respectively [70].

The structures of the complexes $[Ln_2M(CN)_6(bpy)_4(H_2O)_8][M(CN)_6]\cdot8H_2O$ are built up by trinuclear cations $\{[Ln(H_2O)_4(bpy)_2]_2[M(CN)_4(\mu\text{-}CN)_2]\}^{3+}$, an independent anion $[Fe(CN)_6]^{3-}$, and lattice water molecules (Fig. 4) [76,77]. The lanthanide(III) ion is nine-coordinated, being surrounded by four nitrogen atoms of two bpy ligands, one nitrogen atom of the bridging cyanido ligand and four oxygens of water molecules. The coordination polyhedron of the lanthanide(III) ions is a distorted gyroelongated square pyramid polyhedron as indicated by a stereochemical study based on continuous shape measures [77]. The Ln···M intramolecular distances are in the range of 5.538–5.684 Å. The Ln–M–Ln angles fall in the range 179.9–180.0°, indicating a *trans*-configuration imposed by the presence of an inversion center at the transition metal atom. In the crystal lattice, the trinuclear cations are self-assembled through hydrogen bonds giving an extensive three-dimensional network. The hydrogen bonding interactions established between the trinuclear entities and the counter ions result in a two-dimensional network (Fig. 5). Furthermore, these assemblies are interconnected to form a three-dimensional network of hydrogen bonds. Weak intermolecular π–π stacking interactions provide additional stabilization of the crystal structure. Diaz and co-workers [77] have performed magnetic susceptibility studies for the family of complexes $[Ln_2M(CN)_6(bpy)_4(H_2O)_8][M(CN)_6]\cdot8H_2O$ (Ln = La(III), Ce(III), Pr(III), Nd(III), Sm(III); M = Fe(III), Co(III)). However, no significant magnetic interactions were found between the lanthanide(III) ions and the iron(III) ion in these complexes.

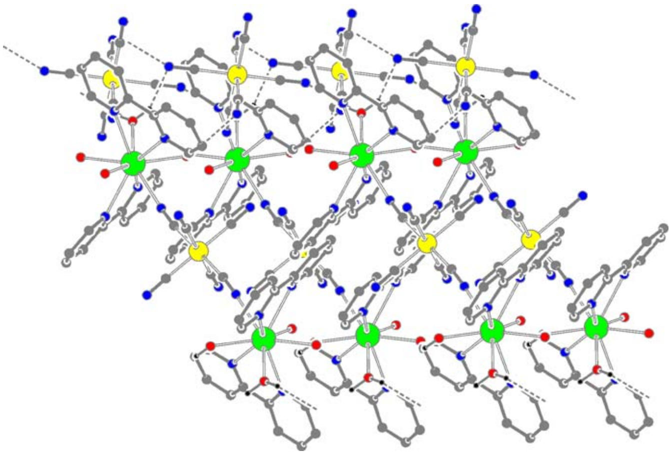

Fig. 5. View of the hydrogen bonding interactions established between the trinuclear entities and the counter ions in $[Nd_2Fe(CN)_6(bpy)_4(H_2O)_8]$-$[Fe(CN)_6]\cdot8H_2O$ [76,77].

2.3. Tetranuclear cyanido-bridged complexes

Attempts to prepare different d–f cyanido-bridged assemblies with diverse monodentate ligands have often illustrated that the types of complexes to be formed are non-predictable. In one case, attempts to synthesize one-dimensional chains using urea as blocking ligand have led to the isolation of the tetranuclear complex $[\{Gd(urea)_4(H_2O)_2\}_2\{Cr(CN)_6\}_2]$ [42]. The complex is a neutral molecular square with two Gd(III) ions linked by two $[Cr(CN)_6]^{3-}$ moieties (Fig. 6). Each $[Cr(CN)_6]^{3-}$ moiety bridges two Gd(III) ions using two cyanido ligands, while each Gd(III) ion links two $[Cr(CN)_6]^{3-}$ units in a *cis*-fashion to form a slightly distorted square with a size of ca. 5.6 Å × 5.0 Å. The Cr–C≡N bonds that are involved in bridging exhibit distortion

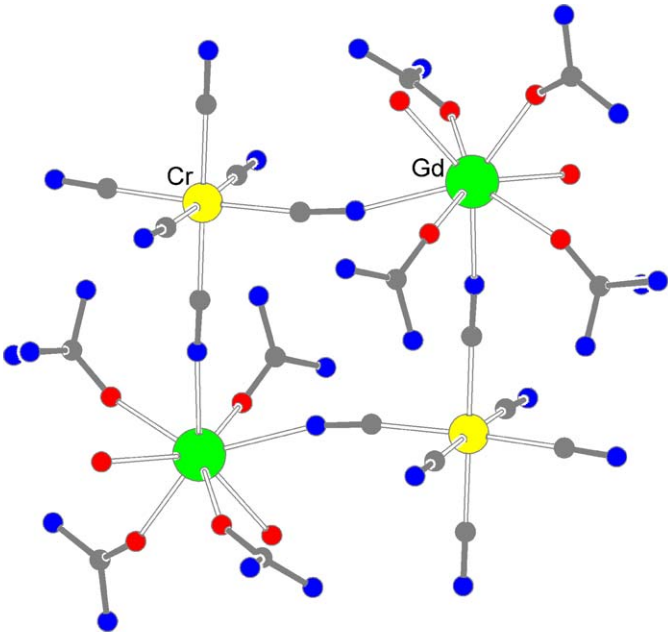

Fig. 6. View of the molecular structure of the tetranuclear complex $[\{Gd(urea)_4(H_2O)_2\}_2\{Cr(CN)_6\}_2]$ [42].

from the linearity (172.3° and 173.9°). The temperature dependence of the magnetic susceptibility suggested the presence of an antiferromagnetic interaction between Cr(III) and Gd(III) ($J_{GdCr} = -0.36\ cm^{-1}$) and weak ferromagnetic intercluster interactions ($zJ' = 0.031\ cm^{-1}$) [42].

Two types of tetranuclear clusters, namely $[Sm_2(OAc)_2(phen)_4(H_2O)_2\{Fe(CN)_5(NO)\}_2]$ and $[Dy_2(OAc)_2(phen)_4(H_2O)_2\{Fe(CN)_5(NO)\}_2]\cdot 8H_2O$ (OAc = acetate; phen = 1,10-phenanthroline), have been obtained by the simultaneous use of cyanido and carboxylate groups as bridging ligands [78]. In the former case, two $[Fe(CN)_5(NO)]^{2-}$ moieties are linked to one Sm(III) ion of a $[Sm_2(OAc)_2]$ unit to form a T-shaped motif. The bridging cyanido ligands coordinate to samarium(III) ion in a bent fashion with the Sm–N≡C bond angle being 163.5°. In the later complex, two $[Fe(CN)_5(NO)]^{2-}$ moieties are linked to both Dy(III) ions of the $[Dy_2(OAc)_2]$ fragment, thus resulting in a U-shaped topology. The bridging cyanido ligands coordinate to dysprosium(III) ions in a slightly bent fashion (Dy–N≡C bond angles of 166.5° and 172.7°, respectively); the Dy···Fe distances are 5.499 and 5.544 Å, respectively.

2.4. One-dimensional cyanido-bridged complexes

Self-assembly of the anionic building-block $[M(CN)_6]^{3-}$ and lanthanide ions in the presence of various blocking ligands have frequently resulted in the formation of one-dimensional chains: (i) $\{[Ln(dmf)_4(H_2O)_2M(CN)_6]\cdot H_2O\}_n$ (Ln = Sm(III), Gd(III), Tb(III), Dy(III), Er(III); M = Cr(III), Mn(III)) [35,39,79,80]; (ii) $\{[Sm(dma)_2(H_2O)_4Fe(CN)_6]\cdot H_2O\}_n$ [70,75] and $\{[Gd(capro)_2(H_2O)_4Cr(CN)_6]\cdot H_2O\}_n$ (capro = caprolactam) [42]; (iii) $\{[Ln(bpy)(H_2O)_4M(CN)_6]\cdot 4H_2O\cdot 1.5bpy\}_n$ (Ln = Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III); M = Fe(III), Co(III)) [38,81]; (iv) $[Ln(bet)_2(H_2O)_3Fe(CN)_6]_n$ (Ln = Nd(III), Pr(III), Sm(III), Gd(III); bet = betaine) [35,82]; (v) $\{[Ce(gly)_3(H_2O)Fe(CN)_6]\cdot H_2O\}_n$ (gly = glycine) [83]. The synthesis of these complexes employs the reaction of the lanthanide(III) salts and $[M(CN)_6]^{3-}$ building-blocks (M = Mn(III), Fe(III), Co(III)) in a 1:1 stoichiometry and in the presence of the corresponding organic ligand (in excess, with respect to Ln(III)).

The first complete characterization of a cyanido-bridged one-dimensional d–f polymer chain, $\{[Gd(dmf)_4(H_2O)_2Cr(CN)_6]\cdot H_2O\}_n$, has been reported by Ribas and co-workers [39]. The crystallographic analysis revealed alternation of Gd(III) and Cr(III) units linked by cyanido bridges in which each $[Gd(dmf)_4(H_2O)]$ unit connects two $[Cr(CN)_6]^{3-}$ moieties in a *cis*-fashion to form a zig-zag chain structure (Fig. 7); the intramolecular Gd···Cr separation is 5.652 Å. The Gd–Cr–Gd angle is 98.4°, thus suggesting a *cis*-geometry for the $[Cr(CN)_6]^{3-}$ unit; the Cr–C≡N of 170.6° indicates a bent cyanide bridge. The Gd(III) ion is eight-coordinated with the coordination sphere being filled by six oxygen atoms of two water molecules and four dmf ligands and two nitrogen atoms of the bridging cyanido ligands. The hydrogen-bonding interactions involving both coordinated and lattice water molecules and the terminal cyanido ligands result in a three-dimensional network structure. Attempts to increase the dimensionality of the cyanido-bridged assemblies by using other monodentate ligands in lower concentration (Ln:ligand = 1:2) have resulted in the formation of the similar one-dimensional assemblies $\{[Gd(capro)_2(H_2O)_4Cr(CN)_6]\cdot H_2O\}_n$ [42] and $\{[Sm(dma)_2(H_2O)_4Fe(CN)_6]\cdot H_2O\}_n$ [70,75].

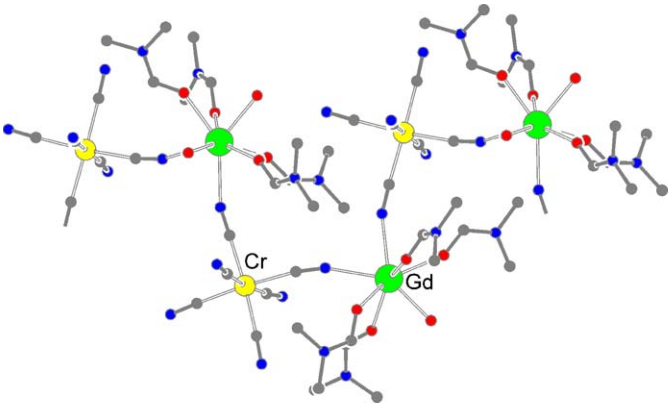

Fig. 7. View of the zig-zag chain molecular structure of $\{[Gd(dmf)_4(H_2O)_2Cr(CN)_6]\cdot H_2O\}_n$ [39].

The magnetic susceptibility data for the complex $\{[Gd(dmf)_4(H_2O)_2Cr(CN)_6]\cdot H_2O\}_n$ revealed a weak antiferromagnetic interaction between Gd(III) and Cr(III) ($J_{GdCr} = -0.52\ cm^{-1}$) [39]. This result is in agreement with those reported by Kou et al. [42] for the tetranuclear complex $[Gd(urea)_4(H_2O)_2]_2[Cr(CN)_6]_2$ that shows a similar magnetic behaviour and Gd···Cr distance. The nature of the magnetic coupling between Sm(III) and Cr(III) ions in the $\{[Sm(dmf)_4(H_2O)_2Cr(CN)_6]\cdot H_2O\}_n$ analogue could not be determined because in this case the magnetic properties are strongly dominated by the first- and second-order Zeeman effect contributions of the ground state ($^6H_{5/2}$) and excited state ($^6H_{7/2}$) of the Sm(III) ion [80]. For the series $\{[Ln(dmf)_4(H_2O)_2Mn(CN)_6]\cdot H_2O\}_n$, the exchange magnetic coupling between Sm(III), Tb(III), Dy(III), Er(III) ions with the Mn(III) ion was found to be weakly antiferromagnetic [35,79]. In particular, the complex $[Er(dmf)_4(H_2O)_2Mn(CN)_6]\cdot H_2O$ exhibits long-range magnetic ordering with a critical temperature T_c of 17.5 K and a relatively strong coercive force ($H_c = 980$ Oe) [79].

The reaction of $Ln(NO_3)_3\cdot xH_2O$ with $K_3[M(CN)_6]$ and bpy in aqueous solutions leads to the formation of one-dimensional cyanido-bridged complexes of formula $\{[Ln(bpy)(H_2O)_4M(CN)_6]\cdot 4H_2O\cdot 1.5bpy\}_n$ [38,81]. In all cases, the one-dimensional chain comprises cyanido-bridged alternating $Ln(bpy)(H_2O)_4$–$M(CN)_6$ fragments (Fig. 8). The

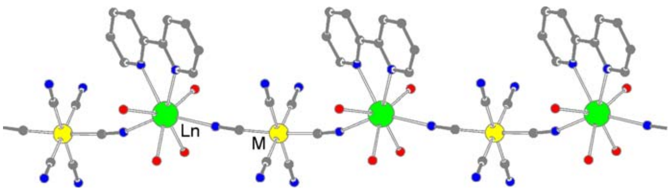

Fig. 8. View of the zig-zag chain structure of $\{[Ln(bpy)(H_2O)_4M(CN)_6]\cdot 4H_2O\cdot 1.5bpy\}_n$ [38,81].

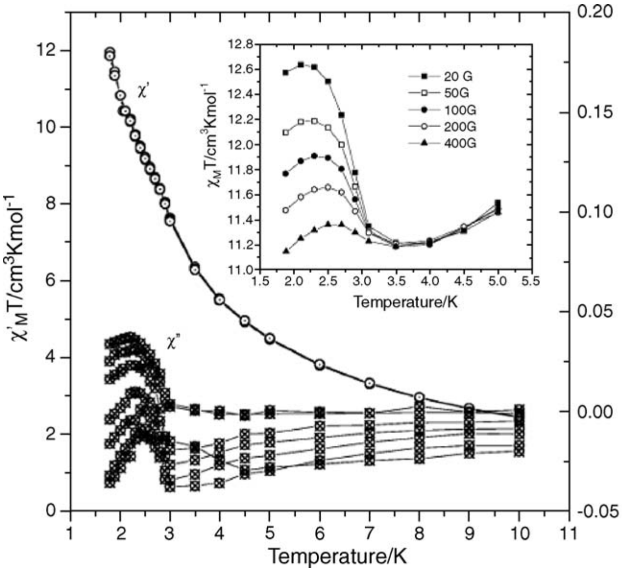

Fig. 9. Plot of the in-phase in out-of-phase of the a.c. magnetic susceptibility of $\{[Dy(bpy)(H_2O)_4Fe(CN)_6]\cdot 4H_2O\cdot 1.5bpy\}_n$. Inset: Temperature dependence of $\chi_M T$ at low magnetic fields [38,81].

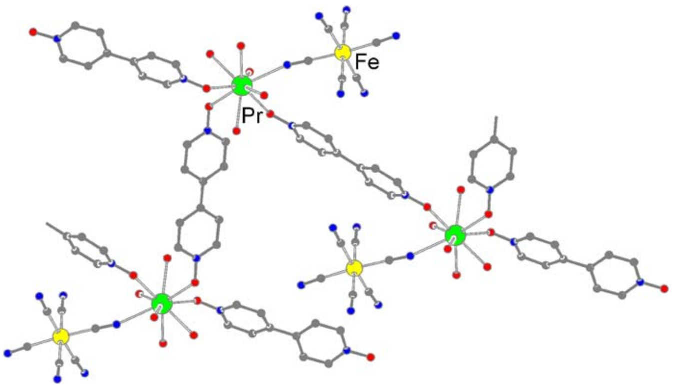

Fig. 10. View of the zig-zag chain structure of $[\{(H_2O)_5(L_1)Pr\text{-}NC\text{-}Fe(CN)_5]\}(\mu\text{-}L_1)]\cdot 0.5L_1\cdot 4H_2O$ (L_1 = 4,4′-dipyridyl-*N*,*N*′-dioxide) [36].

lanthanide(III) ion has a coordination number of eight, being surrounded by four oxygen atoms of four water molecules, two nitrogen atoms of the bpy ligand and two nitrogen atoms of two cyanido bridges. Each $[M(CN)_6]^{3-}$ moiety coordinates to two lanthanide(III) ions using two *trans*-cyanido ligands, while each $Ln(bpy)(H_2O)_4$ group connects two $[M(CN)_6]^{3-}$ moiety in a *cis*-fashion. The Ln–M–Ln angles fall in the range 159.1–159.7°, in agreement with the *trans*-geometry of the $[M(CN)_6]^{3-}$ moiety. The intramolecular Ln···M distances are in the range of 5.421–5.612 Å. The molecular structure is further stabilized by the interplay of hydrogen-bonding and π–π interactions. In this family of complexes, the magnetic exchange coupling between Ln(III) and Fe(III) is found to be antiferromagnetic for Ln = Gd(III), Dy(III), Tb(III), and no significant magnetic interaction has been observed for Eu(III), Ho(III), Er(III), Tm(III). Particularly, the temperature dependence of the $\chi_M T$ values for the complex $\{[Dy(bpy)(H_2O)_4Fe(CN)_6]\cdot 4H_2O\cdot 1.5bpy\}_n$ has indicated that at low temperature the experimental magnetization is lower than that of the uncorrelated spin systems, in agreement with the presence of antiferromagnetic interactions (Fig. 9) [81]. At low magnetic fields, a maximum at 2.5 K is observed in the $\chi_M T$ value. The a.c. magnetic susceptibility shows a small frequency dependence of the peaks, attributed to the glassy behaviour of the magnetic ordered state [81]. A similar behaviour has been observed for the complex $\{[Sm(bpy)(H_2O)_4Fe(CN)_6]\cdot 4H_2O\cdot 1.5bpy\}_n$ [38]. In both cases, zero-field cooled and field-cooled magnetization measurements have suggested the onset of weak long-range ferromagnetic ordering at 2.5 and 3.5 K, respectively [38,81].

Some one-dimensional cyanido-bridged complexes, $[Ln(bet)_2(H_2O)_3Fe(CN)_6]_n$ with Ln = Nd(III), Pr(III), Sm(III), Gd(III), have been obtained in the reaction of $Ln(NO_3)_3\cdot xH_2O$ with $K_3[M(CN)_6]$ and betaine as blocking ligand [35,82]. These complexes have a chain structure through two approximately parallel *trans*-cyanido bridges between lanthanide(III) and iron(III) ions. The Fe–C≡N angles do not significantly deviate from linearity; however, the bridging cyanido ligand is coordinated to the lanthanide(III) ion in a bent mode (Ln–N≡C ∼ 177°), which is attributed to the steric hindrance of the coordinate bet molecules around the lanthanide(III) ion. The hydrogen bonding interactions established between the coordinated water molecules and the bridging cyanido ligands link two adjacent chains to form a two-dimensional network structure. In all cases, the temperature dependence of $\chi_M T$ values suggest weak antiferromagnetic interactions between the lanthanide(III) and iron(III) ions [35,82].

Andruh and co-workers [36] have shown that the simultaneous use of $[M(CN)_6]^{3-}$ building-blocks and *exo*-didentate ligands is an alternative synthetic route for the design of cyanido-bridged one-dimensional assemblies. The reaction of $Pr(NO_3)_3\cdot xH_2O$ with 4,4′-bipyridine-*N*,*N*′-dioxide (L_1) and $K_3[M(CN)_6]$ (M = Fe, Co) yields isomorphous complexes with formula $[\{(H_2O)_5(L_1)Pr\text{-}NC\text{-}M(CN)_5]\}(\mu\text{-}L_1)]\cdot 0.5L_1\cdot 4H_2O$ [36]. The one-dimensional structure is made up by $\{(H_2O)_5(L_1)Pr\text{-}NC\text{-}M(CN)_5]\}$ neutral dinuclear entities, which are bridged by 4,4′-bipyridine-*N*,*N*′-dioxide to form an infinite zig-zag chain (Fig. 10). The interplay of hydrogen bonding and π–π stacking interactions results in a three-dimensional network structure. The temperature-dependent magnetic properties of these complexes are dominated by the first-order orbital contributions of Pr(III) and Fe(III), respectively [36].

2.5. *Two-dimensional cyanido-bridged complexes*

The first two-dimensional d–f network based on cyanido bridges, $[NdM(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ (M = Fe(III), Co(III); bpym = 2,2′-bipyrimidine), has been reported by Song and co-workers [45]. The slow diffusion of $K_3[M(CN)_6]$ and the ligand bpym with $Nd(NO_3)_3$ in a 1:1:1 molar ratio in an aqueous solution results in the formation of a two-dimensional topological architecture in which rhombus-like $Nd_2M_2(CN)_4$ rings and six-sided $Nd_4M_4(CN)_8$ rings are alternating (Fig. 11). Each Nd(III) ion is nine-coordinated with a mono-capped square antiprism coordination geometry, being surrounded by two nitrogen atoms from one chelating bpym molecule,

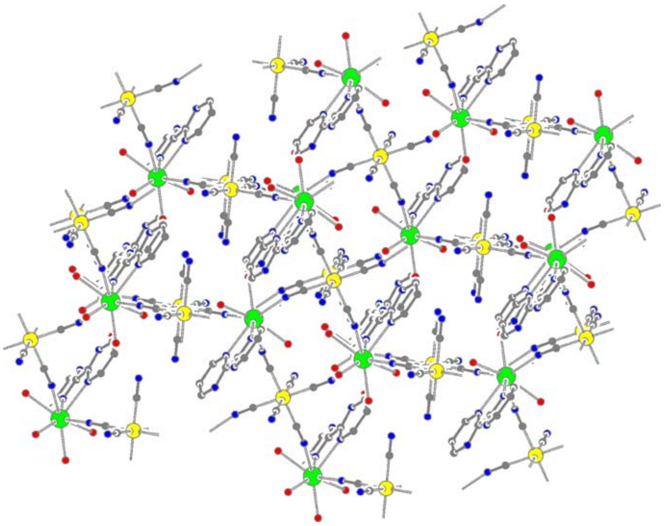

Fig. 11. The two-dimensional topological architecture of $[NdFe(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ [45].

four oxygen atoms from water molecules and three nitrogen atoms from three bridging cyanido ligands. The four equatorial cyanido groups of the $[M(CN)_6]^{3-}$ entities are connected to four Nd(III) ions to form a double strand chain, while the two *trans*-cyanido groups link neighboring chains to form an unusual two-dimensional structure. The bridging cyanido ligands link the Nd(III) ions in a bent fashion with the Nd–N≡C bond angles ranging from 158.5° to 166.1°. The two-dimensional sheets are linked into a three-dimensional network through hydrogen-bonding interactions involving the lattice water molecules [45]. The shortest intralayer Nd···M separation is 5.606 Å, whilst the shortest interlayer Nd···M distance is 8.897 Å. The temperature-dependent magnetic susceptibility measurements for $[NdFe(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ agree with ferromagnetic interactions between the Nd(III) and Fe(III) ions (Fig. 12), but no long-range ordering was detected down to 2 K based on field-dependence magnetization and a.c. magnetic susceptibility studies [45]. Surprisingly, in the case of the isomorphous complex $[NdCo(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$, both in-phase ($\chi'_M$) and out-phase ($\chi''_M$) components are strongly frequency dependent in the zero-field a.c. magnetic susceptibility measurements (Fig. 12). This behaviour was interpreted in terms of an unusual glass-like behaviour, which was attributed to the geometrically frustration of the Nd(III) ions in the crystal lattice [45].

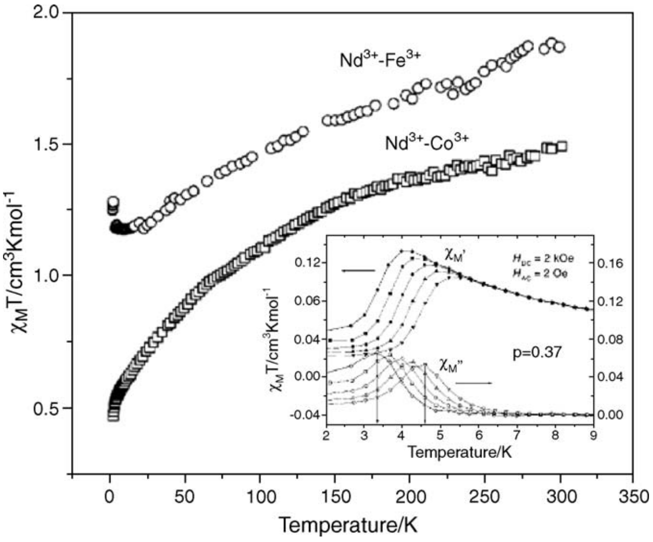

Fig. 12. Temperature dependence of $[NdM(bpym)(H_2O)_4(CN)_6]\cdot 3H_2O$ ((○) for M = Fe and (□) for M = Co). Inset: Frequency dependence of a.c. magnetic susceptibility [45].

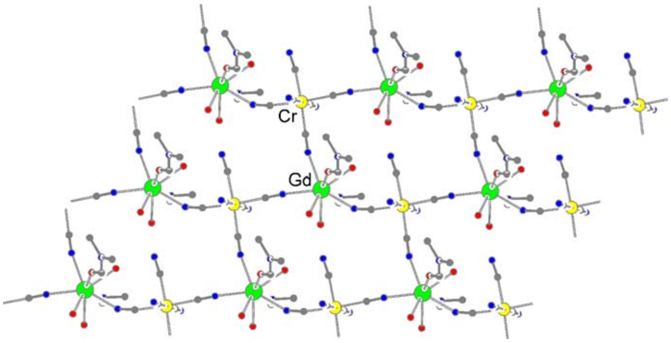

Fig. 13. View of the brick-wall structure of the complex $[Gd(dmf)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$ [84].

The reaction of $Gd(NO_3)_3\cdot n H_2O$, dmf and $K_3[Cr(CN)_6]$ in the molar ratio 1:2:1 in an aqueous solution affords the complex $[Gd(dmf)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$ with a brick-wall-like structure (Fig. 13) [84]. In the crystal lattice, each $[Cr(CN)_6]^{3-}$ unit uses three cyanido groups in a meridional arrangement to connect three $[Gd(dmf)_2(H_2O)_3]^{3+}$ anions, thus forming neutral layers with slightly distorted Gd_3Cr_3 rectangles. The bridging cyanido ligands coordinate to the gadolinium(III) ions in two different fashions: two nearly linear (Gd–N≡C = 174.9° and 167.5°, respectively) and one bent (Gd–N≡C = 154.1°). The adjacent Gd···Cr are in the range 5.469–5.692 Å and the shortest interlayer metal–metal distance is 7.738 Å. The uncoordinated water molecules are positioned between the distantly parallel flat layers and link to one terminal cyanido ligand of $[Cr(CN)_6]^{3-}$ and the coordinated water molecules via hydrogen-bonding. The non-bridging cyanido ligands are hydrogen bonded to coordinated water molecules, thus connecting the layers in a three-dimensional structure. A similar structure has been reported for the complex $[Sm(dmf)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$ [80]. For the isomorphous complex $[Gd(dmf)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$, the plot $\chi_M T$ versus temperature indicates the occurrence of an antiferromagnetic coupling between the Gd(III) and Cr(III) ions, with the $\chi_M T$ decreasing smoothly in the temperature range 300–10 K. With a further decrease in temperature, the $\chi_M T$ value increases sharply and it reaches a maximum of 10.9 $cm^3\,K\,mol^{-1}$ at 4 K before decreasing again (Fig. 14). The abrupt increase of the $\chi_M T$ value around 4 K suggests an intralayer ferromagnetic behaviour as a result of the non-cancellation of spins, while the decrease of the $\chi_M T$ value below 4 K indicates a long-range antiferromagnetic ordering between the ferrimagnetic layers [84]. The magnetization versus field curve has a “double-*S*” shape, which indicates a metamagnet state that switches from an antiferromagnetic ground state to a ferromagnetic-like state upon

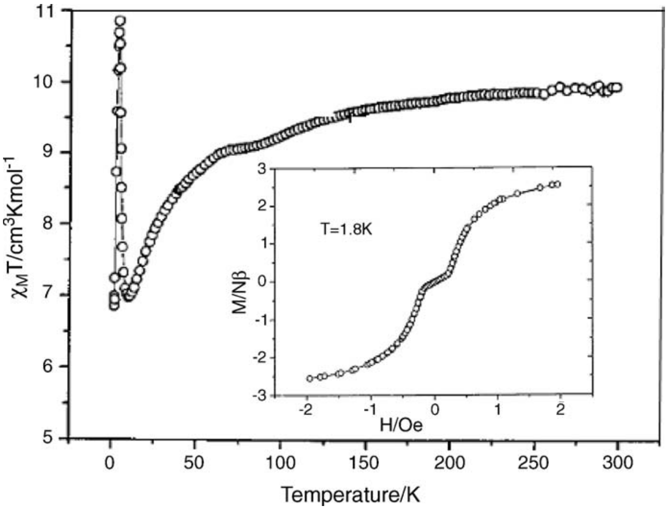

Fig. 14. Temperature dependence of $\chi_M T$ and field dependence of the magnetization (inset) for the complex $[Gd(dmf)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$ [84].

the application of a large field (Fig. 14) [84]. Magnetic studies on $[Sm(dmf)_2(H_2O)_3Cr(CN)_6]\cdot H_2O$ showed a magnetic phase-transition temperature below 4.2 K and a coercive field of 100 Oe at 1.85 K [80].

Recently, Einaga and co-workers [85] reported a new d–f cyanido-bridged heterobimetallic complex, $[Ln(hp)_2(H_2O)_3Fe(CN)_6]_n$ (Ln = Ce(III), Nd(III); hp = 4-hydroxypyridine), with a two-dimensional honeycomb network structure. Photo-induced magnetization studies have shown that upon irradiation at 5 K, the magnetization slightly increased and gradually saturated after several hours. However, by increasing the temperature to 12 K the photo-induced magnetization was erased indicating that that the photo-excited state reached the ground state [85].

3. Heterotrimetallic d–f assemblies

A suitable approach to the synthesis of cyanido-bridged heterotrimetallic systems employs the use of an anionic building-block, $[M(CN)_6]^{3-}$ (M = Cr(III), Fe(III), Co(III)) in conjunction with heterodinuclear {CuGd} complexes with compartmental Schiff-base ligands [46]. Andruh and coworkers [46] have shown that the reaction of the complex [Cu(salpn)] (H_2salpn = *N*,*N*′-propylenedi(3-methoxysalicylideneiminato)) with $Gd(NO_3)_3\cdot xH_2O$, followed by the substitution of the nitrato ligands with $[Fe(CN)_6]^{3-}$ ions affords a trimetallic complex containing three different spin carriers, i.e. $[Cu(salpn)Gd(H_2O)_3\{Fe(CN)_6\}]\cdot 4H_2O$. The polymeric structure of this complex has a ladder topology built up of $\{Gd_2Fe_2Cu\}$ pentagons that share the FeGd edges (Fig. 15). In this topology, each $[Fe(CN)_6]^{3-}$ group connects three heterodinuclear {CuGd} units using three meridionally disposed cyanido ligands. Two cyanido ligands bridge the Gd(III) and Fe(III) ion, whilst the third one connects the Fe(III) and Cu(II) ions. The Cu···Gd distance is 3.508 Å and the two Fe···Gd distances are 5.503 and 5.580 Å, respectively. The hydrogen-bonding interactions involving the coordinated water molecules and cyanido ligands, as well as the lattice water molecules, lead to a three-dimensional network structure. The temperature dependence of the magnetic susceptibility for the isostructural complexes $[Cu(salpn)Gd(H_2O)_3\{M(CN)_6\}]\cdot 4H_2O$ (M = Fe(III), Co(III)) indicated that no magnetic interaction occurs between the heterodinuclear {CuGd} units within the chain, but the heterodinuclear {CuGd} units interact ferromagnetically with the paramagnetic $[Fe(CN)_6]^{3-}$ linkers [46]. The magnetic interaction between Cu(II) and Gd(III) ion is ferromagnetic ($J_{CuGd} = 7.24\ cm^{-1}$).

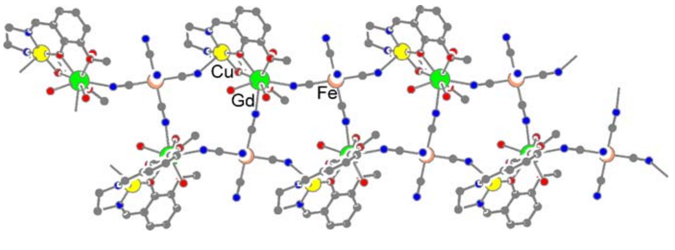

Fig. 15. View of the two-dimensional structure of the complex $[Cu(salpn)Gd(H_2O)_3\{Fe(CN)_6\}]\cdot 4H_2O$ [46].

A series of isostructural heterotrimetallic complexes, $\{[CuL_2]_2Ln(H_2O)_2[M(CN)_6]\}\cdot 7H_2O$ (Ln = La(III), Gd(III); M = Cr(III), Fe(III), Co(III); L_2 = 1,4,8,11-tetra-azacyclotradecane-2,3-dione), has been reported by Kou et al. [43]. These complexes are obtained by self-assembly of $\{CuL_2\}$, $LnCl_3\cdot xH_2O$ and $K_3[M(CN)_6]$ in aqueous solution. The lanthanide(III) ion is eight-coordinated by six oxygen atoms of two $\{CuL_2\}$ units and two water molecules, and two nitrogen atoms of the bridging cyanido ligands of two $[M(CN)_6]^{3-}$ groups. Each $[M(CN)_6]^{3-}$ anion connects two lanthanide(III) ions using two *trans*-cyanido ligands, thus forming a chain-like structure (Fig. 16) [43]. In the chain, each $\{CuL_2\}$ group tilts toward the cyanido ligand of adjacent $[M(CN)_6]^{3-}$ anions. Surprisingly, the self-assembly of $\{CuL_2\}$, $GdCl_3\cdot xH_2O$ and $K_3[Cr(CN)_6]$ in a water–ethanol solution gives the complex $[Gd(CuL_2)_4Cr(CN)_6\cdot 5H_2O]$ that has a grid-like molecular structure [44]. In the crystal lattice, each $[M(CN)_6]^{3-}$ ion connects four different $\{CuL_2\}$ units through four equatorial cyanido ligands. As a result, each Cu(II) ion is five-coordinated with four nitrogen from the blocking ligand located in the equatorial plane and one nitrogen from the cyanido ligand at the apical position. The Gd(III) ion is surrounded by four oxygen atoms from four $\{CuL_2\}$ units [44].

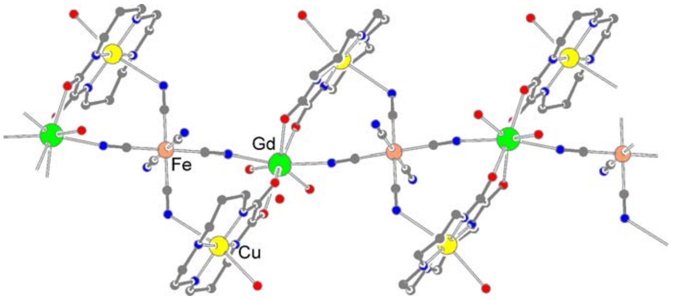

Fig. 16. View of the chain-like molecular structure of $\{[CuL'']_2Gd(H_2O)_2[Fe(CN)_6]\}\cdot 7H_2O$ (L_2 = 1,4,8,11-tetra-azacyclotradecane-2,3-dione) [43,44].

The temperature dependence of the magnetic data for the complex $\{[CuL_2]_2Gd(H_2O)_2[M(CN)_6]\}\cdot 7H_2O$ (M = Fe(III), Co(III)) is consistent with a Cu(II)–Gd(III) ferromagnetic interaction ($J_{CuGd} = 2.21\,cm^{-1}$ for {CuGdCo} and $J_{CuGd} = 0.98\,cm^{-1}$ for {CuGdFe}), upon which an intermolecular antiferromagnetic coupling is imposed. Based on the magnetic data of the complexes $\{[CuL_2]_2La(H_2O)_2[M(CN)_6]\}\cdot 7H_2O$ (M = Cr(III), Fe(III)), it was found that the weak bridging cyanide ligands mediate ferromagnetic interactions between the Cu(II) and Fe(III)/Cr(III) ions ($J_{CuFe} = 1.71\,cm^{-1}$; $J_{CuCr} = 0.50\,cm^{-1}$). In the case of the complex {CuGdCr}, a spin frustration phenomenon is observed due to the concurrence of dominant ferromagnetic Cu(II)–Gd(III), minor antiferromagnetic Gd(III)–Cr(III) and ferromagnetic Cu(II)–Cr(III) magnetic interactions [43,44].

4. Concluding remarks

The present review has outlined the efforts to obtain new magnetic materials based on the self-assembly reactions between $[M(CN)_6]^{3-}$ and lanthanide ions in the presence of a variety of monodentate and didentate organic ligands. The examples presented here illustrate the great variety of structures that can be adopted by the different lanthanide ions in the corresponding cyanido-bridged assemblies. In a few cases, crystal structure analysis of a couple of isostructural d–f cyanido-bridged complexes has been performed in order to determine the spin-coupling mechanism between the lanthanide ions and transition metal ions. However, attempts to make magneto-structural correlations have proved impossible until now, due to the complexity of the d–f magnetic interactions and because of the few complexes reported in the literature with similar Ln-CN-M cores. Notably, $[M(CN)_6]^{4-}$ ions have not received attention as possible precursors for the synthesis of d–f polymetallic assemblies. The design of new d–f cyanido-bridged magnetic materials is likely to be boosted by exploring the versatility of the octacyanidometallate building-block $[M(CN)_8]^{n-}$ (M = Mo, W, Nb) for the self-assembly of novel supramolecular coordination compounds. An appropriate combination of magnetic centers along with the larger extension of the 4d or 5d magnetic orbitals and different geometries of the $[M(CN)_8]^{n-}$ anions may lead to very interesting magnetic and optical properties in the d–f extended systems [86].

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References

[1] Y. Rodriguez-Martin, M. Hernandez-Molina, F.S. Delgado, J. Pasan, C. Ruiz-Perez, J. Sanchiz, F. Lloret, M. Julve, Cryst. Eng. Commun. (2002) 522.
[2] J.V. Yakhmi, Physica B 321 (2002) 204.
[3] G. Schwarzenbacher, B. Evers, I. Schneider, A. de Raadt, J. Besenhard, R. Saf, J. Mater. Chem. 12 (2002) 534.
[4] J.M. Rawson, G.D. McManus, Coord. Chem. Rev. 189 (1999) 135.
[5] W.R. Entley, C.R. Treadway, G.S. Girolami, Mol. Cryst. Liq. Cryst. 273 (1995) 153.
[6] W.R. Entley, G.S. Girolami, Science 268 (1995) 397.
[7] G. Allinson, R.J. Bushby, J.L. Paillaud, J. Mater. Sci. Mater. Electron. 5 (1994) 67.
[8] V. Marvaud, J.M. Herrera, T. Barilero, F. Tuyeras, R. Garde, A. Scuiller, C. Decroix, M. Cantuel, C. Desplanches, Mon. Chem. 134 (2003) 149.
[9] J. Cernak, M. Orendac, I. Potocnak, J. Chomic, A. Orendacova, J. Skorsepa, A. Feher, Coord. Chem. Rev. 224 (2002) 51.
[10] B. Yan, Z.D. Chen, Prog. Nat. Sci. 11 (2001) 401.
[11] M. Pilkington, S. Decurtins, Chimia 54 (2000) 593.
[12] M. Ohba, H. Okawa, Coord. Chem. Rev. 198 (2000) 313.
[13] H. Vahrenkamp, A. Geiss, G.N. Richardson, J. Chem. Soc. Dalton Trans. (1997) 3643.
[14] H. Okawa, M. Ohba, ACS Symp. Ser. 644 (1996) 319.
[15] C.E. Plecnik, S.M. Liu, S.G. Shore, Accounts Chem. Res. 36 (2003) 499.
[16] G. Rogez, E. Riviere, T. Mallah, C. R. Chim. 6 (2003) 283.
[17] A. Bleuzen, V. Escax, J.P. Itie, P. Munsch, M. Verdaguer, C.R. Chim. 6 (2003) 343.
[18] R.J. Parker, L. Spiccia, B. Moubaraki, K.S. Murray, D.C.R. Hockless, A.D. Rae, A.C. Willis, Inorg. Chem. 41 (2002) 2489.
[19] A. Rodriguez-Fortea, P. Alemany, S. Alvarez, E. Ruiz, A. Scuiller, C. Decroix, V. Marvaud, J. Vaissermann, M. Verdaguer, I. Rosenman, M. Julve, Inorg. Chem. 40 (2001) 5868.
[20] M. Verdaguer, A. Bleuzen, C. Train, R. Garde, F.F. de Biani, C. Desplanches, Philos. Trans. R. Soc. Lond. Ser. A: Math. Phys. Eng. Sci. 357 (1999) 2959.
[21] M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scuiller, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier, F. Villain, Coord. Chem. Rev. 192 (1999) 1023.
[22] S. Ferlay, T. Mallah, R. Ouahes, P. Veillet, M. Verdaguer, Inorg. Chem. 38 (1999) 229.
[23] K. VanLangenberg, S.R. Batten, K.J. Berry, D.C.R. Hockless, B. Moubaraki, K.S. Murray, Inorg. Chem. 36 (1997) 5006.
[24] M. Ohba, H. Okawa, Mol. Cryst. Liq. Cryst. 285 (1996) 423.
[25] S. Ferlay, T. Mallah, R. Ouahes, P. Veillet, M. Verdaguer, Nature 378 (1995) 701.
[26] O. Hatlevik, W.E. Buschmann, J. Zhang, J.L. Manson, J.S. Miller, Adv. Mater. 11 (1999) 914.
[27] S.M. Holmes, G.S. Girolami, J. Am. Chem. Soc. 121 (1999) 5593.
[28] O. Sato, Y. Einaga, A. Fujishima, K. Hashimoto, Inorg. Chem. 38 (1999) 4405.
[29] Y. Einaga, S. Ohkoshi, O. Sato, A. Fujishima, K. Hashimoto, Chem. Lett. (1998) 585.
[30] Z.Z. Gu, O. Sato, T. Iyoda, K. Hashimoto, A. Fujishima, Chem. Mater. 9 (1997) 1092.
[31] S. Ohkoshi, S. Yorozu, O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, Appl. Phys. Lett. 70 (1997) 1040.
[32] S. Ohkoshi, O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, Inorg. Chem. 36 (1997) 268.
[33] O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, Science 272 (1996) 704.
[34] O. Sato, T. Iyoda, A. Fujishima, K. Hashimoto, Science 271 (1996) 49.
[35] B. Yan, Z.D. Chen, S.X. Wang, S. Gao, Chem. Lett. (2001) 350.
[36] S. Tanase, M. Andruh, A. Muller, M. Schmidtmann, C. Mathoniere, G. Rombaut, Chem. Commun. (2001) 1084.
[37] A. Figuerola, C. Diaz, J. Ribas, V. Tangoulis, J. Granell, F. Lloret, J. Mahia, M. Maestro, Inorg. Chem. 42 (2003) 641.
[38] A. Figuerola, C. Diaz, J. Ribas, V. Tangoulis, C. Sangregorio, D. Gatteschi, M. Maestro, J. Mahia, Inorg. Chem. 42 (2003) 5274.
[39] A. Figuerola, C. Diaz, M.S. El Fallah, J. Ribas, M. Maestro, J.E. Mahia, Chem. Commun. (2001) 1204.
[40] S. Gao, B.Q. Ma, Z.M. Wang, T. Yi, C.S. Liao, C.H. Yan, G.X. Xu, Mol. Cryst. Liq. Cryst. Sci. Technol. A: Mol. Cryst. Liq. Cryst. 334 (1999) 913.
[41] R. Koner, M.G.B. Drew, A. Figuerola, C. Diaz, S. Mohanta, Inorg. Chim. Acta 358 (2005) 3041.

[42] H.Z. Kou, S. Gao, C.H. Li, D.Z. Liao, B.C. Zhou, R.J. Wang, Y. Li, Inorg. Chem. 42 (2002) 4756.
[43] H.Z. Kou, B.C. Zhou, R.J. Wang, Inorg. Chem. 42 (2003) 7658.
[44] H.Z. Kou, B.C. Zhou, S. Gao, R.J. Wang, Angew. Chem. Int. Ed. 42 (2003) 3288.
[45] B.Q. Ma, S. Gao, G. Su, G.X. Xu, Angew. Chem. Int. Ed. 40 (2001) 434.
[46] R. Gheorghe, M. Andruh, J.-P. Costes, B. Donnadieu, Chem. Commun. (2003) 2778.
[47] B. Du, E.A. Meyers, S.G. Shore, Inorg. Chem. 39 (2000) 4639.
[48] B. Du, E.A. Meyers, S.G. Shore, Inorg. Chem. 40 (2001) 4353.
[49] B. Du, E.R. Ding, E.A. Meyers, S.G. Shore, Inorg. Chem. 40 (2001) 3637.
[50] D.W. Knoeppel, S.G. Shore, Inorg. Chem. 35 (1996) 1747.
[51] D.W. Knoeppel, J.P. Liu, E.A. Meyers, S.G. Shore, Inorg. Chem. 37 (1998) 4828.
[52] J.P. Liu, E.A. Meyers, S.G. Shore, Inorg. Chem. 37 (1998) 5410.
[53] J.P. Liu, E.A. Meyers, J.A. Cowan, S.G. Shore, Chem. Commun. (1998) 2043.
[54] J.P. Liu, D.W. Knoeppel, S.M. Liu, E.A. Meyers, S.G. Shore, Inorg. Chem. 40 (2001) 2842.
[55] S.M. Liu, E.A. Meyers, S.G. Shore, Angew. Chem. Int. Ed. 41 (2002) 3609.
[56] A. Rath, E. Aceves, J. Mitome, J. Liu, U.S. Ozkan, S.G. Shore, J. Mol. Catal. A: Chem. 165 (2001) 103.
[57] S.G. Shore, D.W. Knoeppel, H.B. Deng, J.P. Liu, J.P. White, S.H. Chun, J. Alloy Compd. 249 (1997) 25.
[58] D.F. Mullica, P.K. Hayward, E.L. Sappenfield, Inorg. Chim. Acta 253 (1996) 97.
[59] D.F. Mullica, P.K. Hayward, E.L. Sappenfield, Inorg. Chim. Acta 244 (1996) 273.
[60] D.F. Mullica, F.H. Alvarez, E.L. Sappenfield, J. Solid State Chem. 129 (1997) 12.
[61] D.F. Mullica, J.M. Farmer, J.A. Kautz, Inorg. Chem. Commun. 2 (1999) 73.
[62] F. Hulliger, M. Landolt, H. Vetsch, J. Solid State Chem. 18 (1976) 307.
[63] F. Hulliger, M. Landolt, H. Vetsch, J. Solid State Chem. 18 (1976) 283.
[64] H.Z. Kou, G.M. Yang, D.Z. Liao, P. Cheng, Z.H. Jiang, S.P. Yan, X.Y. Huang, G.L. Wang, J. Chem. Crystallogr. 28 (1998) 303.
[65] D.F. Mullica, J.M. Farmer, B.P. Cunningham, J.A. Kautz, J. Coord. Chem. 49 (2000) 239.
[66] G.M. Li, T. Akitsu, O. Sato, Y. Einaga, J. Coord. Chem. 57 (2004) 855.
[67] G.M. Li, T. Akitsu, O. Sato, Y. Einaga, J. Coord. Chem. 57 (2004) 189.
[68] J.A. Kautz, D.F. Mullica, B.P. Cunningham, R.A. Combs, J.M. Farmer, J. Mol. Struct. 523 (2000) 175.
[69] X.R. Sun, Z.D. Chen, F. Yan, S. Gao, K.K. Cheung, K.M. Che, X. Zhang, J. Cluster Sci. 13 (2002).
[70] B. Yan, Z. Chen, Helv. Chim. Acta 84 (2001) 817.
[71] K.R. Dunbar, R.A. Heintz, Progr. Inorg. Chem. 45 (1997) 283.
[72] G.M. Li, T. Akitsu, O. Sato, Y. Einaga, J. Am. Chem. Soc. 125 (2003) 12396.
[73] G.M. Li, O. Sato, T. Akitsu, Y. Einaga, J. Solid State Chem. 177 (2004) 3835.
[74] G.M. Li, T. Akitsu, O. Sato, Y. Einaga, Hyperfine Interact. 156 (2004) 143.
[75] B. Yan, Z. Chen, Chem. Lett. 29 (2001) 1244.
[76] T. Yi, S. Gao, X.W. Chen, C.H. Yan, B.G. Li, Acta Crystallogr. C: Cryst. Struct. Commun. 54 (1998) 41.
[77] A. Figuerola, J. Ribas, M. Llunell, D. Casanova, M. Maestro, S. Alvarez, C. Diaz, Inorg. Chem. 44 (2005) 6939.
[78] S. Gao, B.Q. Ma, H.L. Sun, J.R. Li, J. Solid State Chem. 171 (2003) 201.
[79] B. Yan, Z.D. Chen, S.X. Wang, Transit. Met. Chem. 26 (2001) 287.
[80] H.Z. Kou, S. Gao, X.L. Jin, Inorg. Chem. 40 (2001) 6295.
[81] A. Figuerola, J. Ribas, D. Casanova, M. Maestro, S. Alvarez, C. Diaz, Inorg. Chem. 44 (2005) 6949.
[82] B. Yan, H.D. Wang, Z.D. Chen, Polyhedron 20 (2001) 591.
[83] S. Garcia-Granda, A.D. Morales, E.R. Ruiz, J.F. Bertran, Acta Crystallogr. C: Cryst. Struct. Commun. 52 (1996) 1679.
[84] H.Z. Kou, S. Gao, B.W. Sun, J. Zhang, Chem. Mater. 13 (2001) 1431.
[85] G.M. Li, P.F. Yan, O. Sato, Y. Einaga, J. Solid State Chem. 178 (2005) 36.
[86] S. Ikeda, T. Hozumi, K. Hashimoto, S. Ohkoshi, J. Chem. Soc. Dalton Trans. (2005) 2120.