Oligonuclear complexes as tectons in crystal engineering: structural diversity and magnetic properties†

Marius Andruh*

Received (in Cambridge, UK) 21st November 2006, Accepted 25th January 2007
First published as an Advance Article on the web 16th February 2007
DOI: 10.1039/b616972d

This article focuses on the employment of bi- and trinuclear complexes as building blocks in designing novel heterometallic systems. A large variety of polynuclear complexes, ranging from high-nuclearity clusters to high-dimensionality coordination polymers, can be constructed by taking advantage of the high flexibility of the multimetallic nodes. The following oligonuclear complexes are currently used as tectons in our laboratory: (a) bis(alkoxo)-bridged copper(II) species; (b) homobinuclear species with metal ions held together by end-off, or macrocyclic compartmental ligands; (c) heterometallic complexes with dissymmetric compartmental ligands. The 3d–4f nodes are particularly interesting since the metal ions interact selectively with various spacers. The intra-node exchange interactions, as well as those between the resulting spins, generate interesting magnetic properties.

Introduction

A significant part of supramolecular chemistry, currently referred to as metallosupramolecular chemistry, is based upon metal ion-directed self-assembly processes.[1] The metal ions, through their stereochemical and electronic predilections, play a key role in controlling the assembly of the molecular components into well-defined architectures. These can be either discrete or infinite structures. The metal ions exert a *structural* role (directing and sustaining the solid-state architecture), and a *functional* one (carrying magnetic, optical, or redox properties). Aiming at obtaining inorganic–organic hybrid materials with new properties and functions, metallosupramolecular chemistry makes an important contribution to the spectacular development of crystal engineering.[2]

The ultimate goal of crystal engineering is to design solids with technologically useful functionalities (molecular magnetic materials, conducting solids, zeolite-like materials, catalysts, luminescent materials, *etc.*).[3] Appropriate synthetic routes are needed in order to control the dimensionality and the network topology, which are crucial factors in determining the physical and chemical properties of the resulting materials.

Originating from Robson's seminal papers published in 1990,[4] the node-and-spacer approach became a paradigm for the construction of a large variety of coordination polymers. It relies upon the strong directionality of the coordination bonds established between the metal ions (nodes, connectors) and the *exo*-dentate ligands (spacers, linkers). The desired network topology can be achieved by choosing the appropriate metal ion (coordination number and geometry, charge, HSAB behaviour) and a suitable designed bridging ligand (denticity, shape, size, HSAB behaviour). In the language of supramolecular chemistry, the spacer is a programmed species, whose encoded information is read by the metal ions according to their coordination algorithm.[5] Furthermore the final architecture can be influenced by ancillary ligands attached to the metal ions.

Coordination polymers can be constructed from oligonuclear nodes as well. The metal ions interact with the divergent ligand through their easily accessible coordination sites. The presence of two or more metal ions confers on the node a higher geometrical flexibility. Moreover, the metal–metal intra- and inter-node interactions can lead to new redox, electric or magnetic properties.

The incorporation of the oligonuclear complexes into extended frameworks occurs through: (i) formation of the

---

University of Bucharest, Faculty of Chemistry, Inorganic Chemistry Laboratory, Str. Dumbrava Rosie nr. 23, 020464-Bucharest, Romania. E-mail: marius.andruh@dnt.ro

† Dedicated to Professor Michel Verdaguer on the occasion of his 65th birthday.

Marius Andruh

Marius Andruh (b. 1954) is Chair of the Inorganic Chemistry Department at the University of Bucharest and Professor in Coordination Chemistry. He studied Chemistry at the University of Bucharest and received his doctorate in 1988, under the supervision of the late Professor Maria Brezeanu. He spent one year as a post-doc in Orsay with Professor Olivier Kahn and one and a half years in Göttingen, as an Alexander von Humboldt fellow, in the group of Professor Herbert W. Roesky. His major research interests are focused on metallosupramolecular chemistry, molecular magnetism and crystal engineering. He is a corresponding member of the Romanian Academy (2001) and member of the Academia Europaea (2004). In 2006 he was awarded the Gauss Professorship of the Akademie der Wissenschaften zu Göttingen.

nodes in a preliminary step, followed by the reaction with appropriate spacers; (ii) formation of the nodes as a result of the interaction of the metal ions with the spacer; (iii) serendipitous assembly of the metal ions into clusters which are then interconnected by spacer molecules. In the second case the formation of the nodes exploits the particular chemical behaviour of some metal ions – for example the assembly of the binuclear paddlewheel motif, with or without metal–metal bonds, that is characteristic of the carboxylates of Cu^{II}, Cr^{II}, Mo^{II}, W^{II}, Rh^{II}, Ru^{II}, *etc*. The replacement of the monocarboxylato ion with a polycarboxylato one leads to the polymerization of the binuclear nodes into extended networks. Metal–metal bonded nodes were extensively employed by Cotton, Lin and Murillo.[6] They have combined two types of linkers: equatorial (polycarboxylato ions generating and connecting the bimetallic nodes) and axial (nitrogen-containing molecules which coordinate into the axial positions of the bimetallic nodes, increasing the dimensionality of the network). A spectacular chemistry was developed by Yaghi *et al.* by taking advantage of the formation of carboxylato-bridged copper(II) or zinc(II) nodes.[7] For example, the copper acetate or the zinc basic acetate structures have been expanded into 3-D networks by the divergent terephthalato ligand, resulting in robust metal–organic frameworks with high porosity and zeolite-like behaviour.[8]

Let us come back to the first synthetic approach mentioned above: preliminary formation of the nodes and subsequent interaction with the bridging ligands. Such nodes can be (Scheme 1): (a) classical paddlewheel species, with or without metal–metal bonds, the two metal ions being bridged by *syn–syn* carboxylato groups (**I**);[9] particularly interesting in this category are the $[Ru^{II}Ru^{III}(OOCR)_4]^+$ mixed-valence species, which, due to their unpaired electrons, have been employed as building blocks in designing original 3-D molecule-based magnets (the linking groups are paramagnetic $[M(CN)_6]^{3-}$ ions, with M = Fe, Cr);[10] (b) homobinuclear species with metal ions held together by end-off, or macrocyclic compartmental ligands (**II**, **III**);[11] (c) heterometallic complexes with dissymmetric compartmental ligands (**IV**, **V**, **VI**);[12] (d) bis(hydroxo)- and bis(alkoxo)-bridged copper(II) species (**VII**, **VIII**).[13]

This article focuses on the structural diversity of heterometallic assemblies, which are obtained by using homo- and heteronuclear cationic species as nodes.

Heterometallic assemblies constructed from homobinuclear nodes and metal-containing spacers

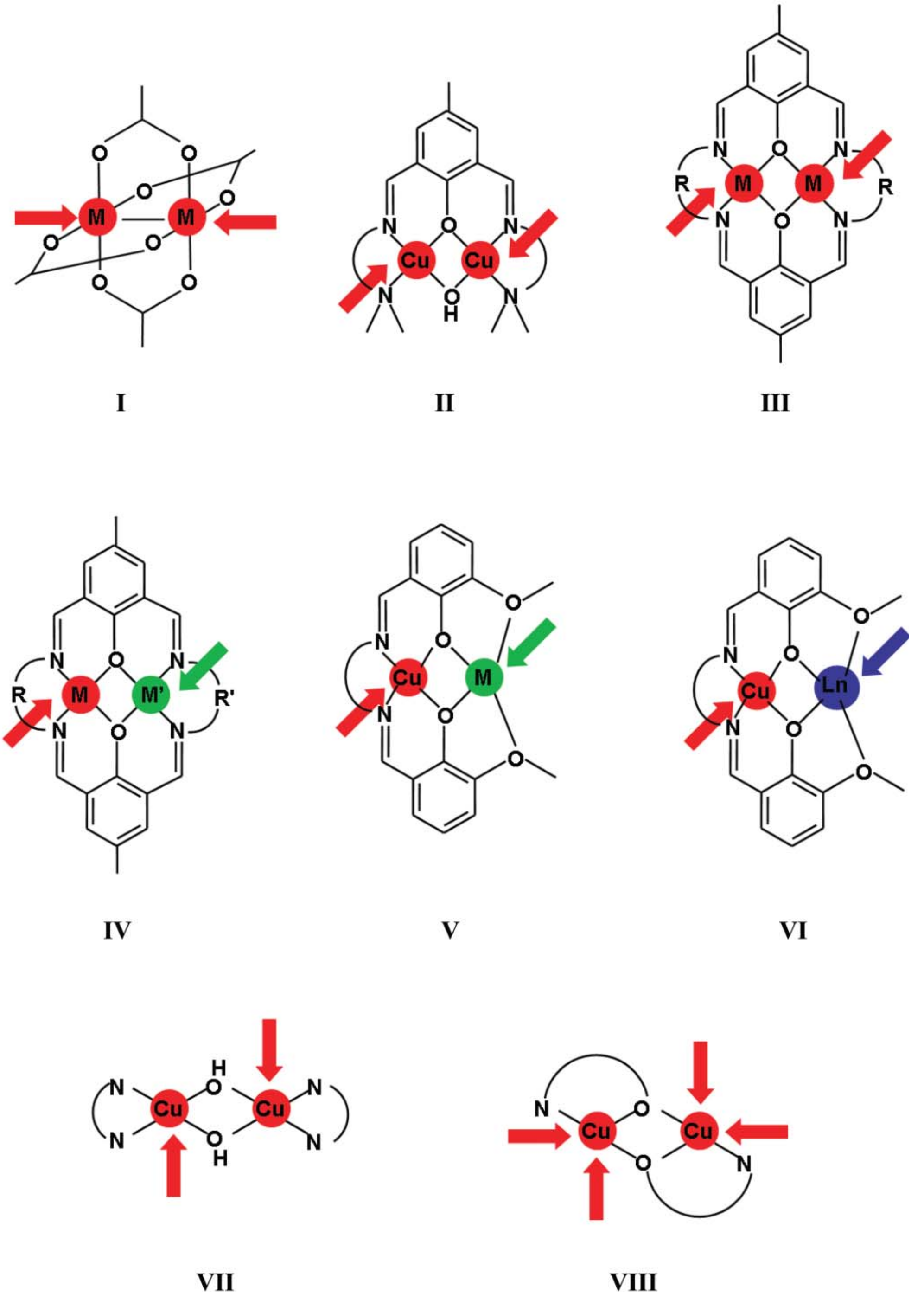
When homometallic nodes are employed to construct heterometallic systems, the spacers (anionic complexes with potentially bridging ligands) must carry the second metal ion.

The alkoxo-bridged copper(II) dimers, **VIII**, act efficiently as nodes. They are spontaneously generated by reacting a copper salt with an aminoalcohol: monoethanolamine (Hmea), propanolamine (Hpa), diethanolamine (H_2dea), triethanolamine (H_3tea), *etc*. The lower the denticity of the aminoalcohol, the higher the dimensionality of the resulting coordination polymer.[12,13b,c] Bidentate aminoalcohols are suited to the construction of 2-D coordination polymers. For example, the reaction between copper tetrafluoroborate and propanolamine, followed by the addition of $K[Au(CN)_2]$ leads to $^{2}_{\infty}[\{Cu_2(pa)_2\}\{Au(CN)_2\}_2]$ **1**.[14] Its crystal structure consists of 2-D layers formed by connecting the $[Cu_2(pa)_2]^{2+}$ centrosymmetric nodes through linear $[Au(CN)_2]^-$ linkers. The coordination geometry of the copper(II) ions is distorted square-pyramidal. Each binuclear node interacts through four $[M(CN)_2]^-$ linkers with four other binuclear nodes. Infinite 2-D chicken-wire sheets are formed (Fig. 1a). The packing of the layers in the crystal is driven by the strong aurophilic interactions (Au···Au = 3.069 Å) established between the gold atoms from different layers. The parallel layers are stacked with offset: the gold atoms from one layer are disposed exactly above the gold atoms from another layer (Fig. 1b).

Three-dimensional coordination polymers based on the same type of binuclear nodes can be obtained by increasing the number of cyano groups in the linker. Indeed, the assembly of $[Cu_2(pa)_2]^{2+}$ and $[Ni(CN)_4]^{2-}$ ions affords a 3-D coordination polymer, $[\{Cu_2(pa)_2\}\{Ni(CN)_4\}]$ **2** (Fig. 2).[14]

An interesting case is the one observed with the Cu(II)–monoethanolamine–$[Au(CN)_2]^-$ system, when the heterometallic complex $^{3}_{\infty}[\{Cu_4(mea)_4\}\{Au(CN)_2\}_4 \cdot H_2O]$ **3** is obtained.[14] Compound **3** is constructed from tetranuclear $\{Cu_4(mea)_4\}$ nodes connected through $[Au(CN)_2]^-$ spacers. It is already known that $\{Cu^{II}{}_4O_4\}$ heterocubane cores can be assembled with monoethanolamine derivatives.[15] The pseudotetrahedral disposition of the copper ions within the node as well as the linearity of the spacer, $[Au(CN)_2]^-$, fulfils the necessary condition for the construction of a diamondoid topology (Fig. 3). The $\{Cu^{II}{}_4O_4\}$ heterocubane moiety can act as a tetrahedral synthon (Fig. 3a). As expected, a 3-D diamondoid net is assembled. The analysis of the packing diagram reveals a four-fold interpenetration of the diamondoid networks (Fig. 4a). Again, the aurophilic interactions intervene in sustaining the supramolecular architecture. Apart from the $[Au(CN)_2]^-$ groups acting as linkers, there are two $[Au(CN)_2]^-$ groups per tetranuclear cluster, which act as terminal ligands. The interpenetrating diamondoid nets are connected through aurophilic interactions established between the dangling $[Au(CN)_2]^-$ ligands from adjacent nets. Infinite chains of gold atoms are thus formed (Fig. 4b). This is a unique case of four-fold interpenetrating nets that are interconnected through aurophilic interactions. The cryomagnetic investigation of **3** revealed a gradual increase, followed by a decrease of the $\chi_M T$ product as the temperature is lowered. A superposition of ferro- (J_1 = +20.8 cm^{-1}) and antiferromagnetic (J_2 = −6.4 cm^{-1}) interactions within the tetranuclear node was found.

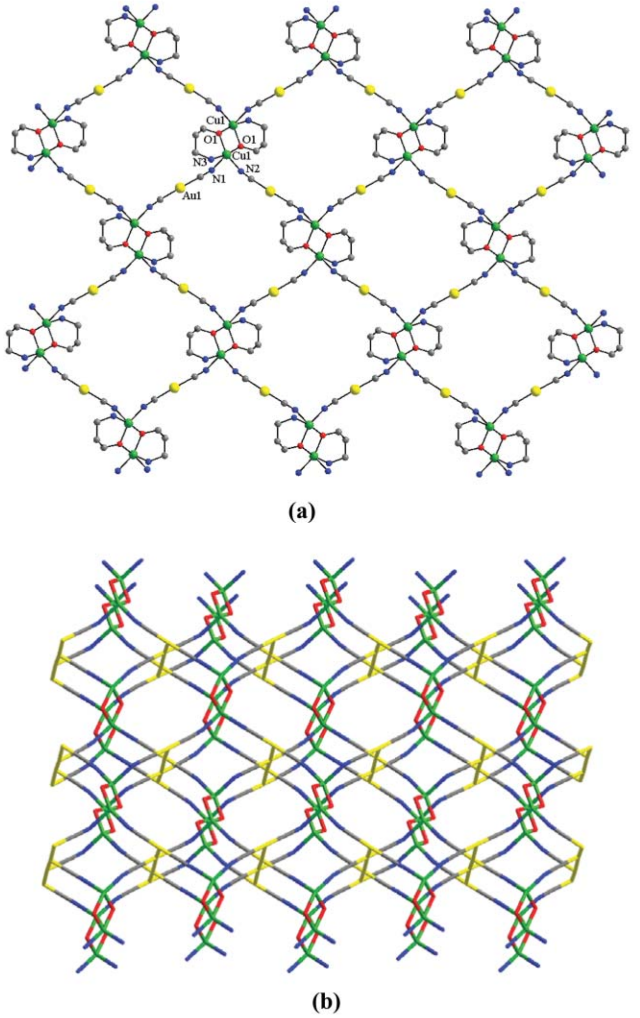
Let us switch now to another type of homobinuclear node, **III**. The metal ions can interact through their axial positions with a large variety of ligands, including metalloligands. The self-assembly processes involving the nickel derivative, $[Ni_2LCl_2] \cdot 2H_2O$, and $[M(bipy)(CN)_4]^-$ (M = Fe, Cr),[16a] or Reinecke anions, *trans*-$[Cr(NH_3)_2(NCS)_4]^-$,[16b] afford [MNiNiM] tetranuclear complexes (the macrocyclic ligand, H_2L, is obtained by reacting 2,6-diformyl-*p*-cresol with 1,3-propanediamine). Their magnetic behaviour results from the exchange interactions between Ni–Ni and Ni–M ions. The molecular structure of one of these complexes, $[\{Ni_2L(H_2O)_2\}\{Cr(NCS)_4(NH_3)_2\}_2] \cdot 2H_2O$ **4**, is shown in



Scheme 1

Fig. 5. The coupling between Cr^{III} and Ni^{II} ions in **4**, both in octahedral stereochemistry, is expected to be ferromagnetic, this pair of ions being a classical example of orthogonality of the magnetic orbitals. However, the simulation of the magnetic data indicates an antiferromagnetic Ni–Cr interaction, with $J_{NiCr} = -22.7\ \mathrm{cm}^{-1}$. This behaviour is explained by the acute Ni–S–C angle [106.03(8)°]. The ferromagnetic interaction is maximal for a linear Ni–SCN–Cr bridging angle. By decreasing this angle, the ferromagnetic interaction decreases also, being finally dominated by the antiferromagnetic one. As far as the Ni–Ni exchange interaction is concerned ($J_{NiNi} = -51.3\ \mathrm{cm}^{-1}$) it falls in the range already observed with several other binuclear nickel complexes with the same ligand.[16]

Reinecke anion derivatives, *trans*-$[Cr(NCS)_4A_2]^-$, can be obtained by replacing the ammonia groups with potentially bridging ligands, *e.g.* pyrazine, 4,4′-bipyridine, *etc*. Such complexes are very appealing as building blocks, since they combine both hard (N) and soft coordination sites (S). The reaction between $K[Cr(NCS)_4(4,4'\text{-bipy})_2]$ and $[Ni_2LCl_2]\cdot 2H_2O$ affords the heterometallic compound $^1_\infty[\{LNi_2(H_2O)_2\}\{Cr(NCS)_4(4,4'\text{-bipy})_2\}]_n\cdot n[Cr(NCS)_4(4,4'\text{-bipy})_2]$ **5**,[16b] which contains infinite



(a)

(b)

Fig. 1 (a) Perspective view of a layer in **1**. (b) Packing diagram for **1** showing the Au···Au contacts. For the sake of clarity the organic ligands are omitted.

cationic chains, constructed from binuclear [Ni–Ni] platforms connected through *trans*-[Cr(NCS)$_4$(4,4′-bipy)$_2$]$^-$ spacers (Fig. 6), and uncoordinated *trans*-[Cr(NCS)$_4$(4,4′-bipy)$_2$]$^-$ ions.

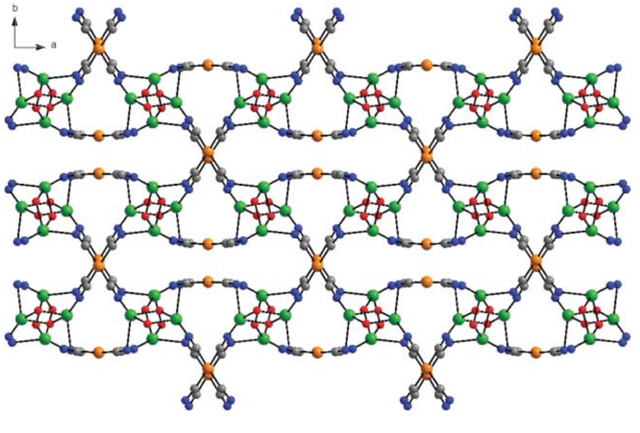
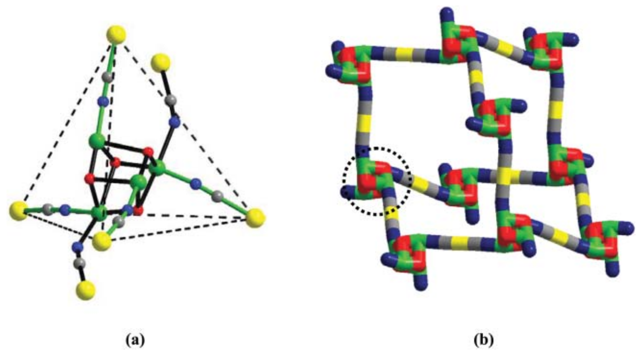


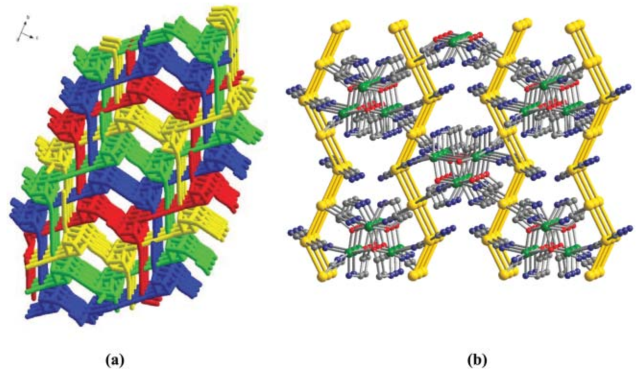
Fig. 2 The 3-D architecture of compound **2**. Colour code: Cu – green; Ni – orange; N – blue; O – red; and C – grey.



(a)

(b)

Fig. 3 (a) The tetrahedral synthon in compound **3**. (b) Illustration of an adamantane-like unit in the structure of **3**; one tetranuclear node is highlighted. For clarity, the carbon atoms from organic ligands as well as water molecules have been removed. Colour code: Cu – green; N – blue; O – red; Au – yellow; and C – grey.



(a)

(b)

Fig. 4 Packing diagram for compound **3**, showing (a) the four-fold interpenetration; (b) the aurophilic interactions connecting the interpenetrating nets.

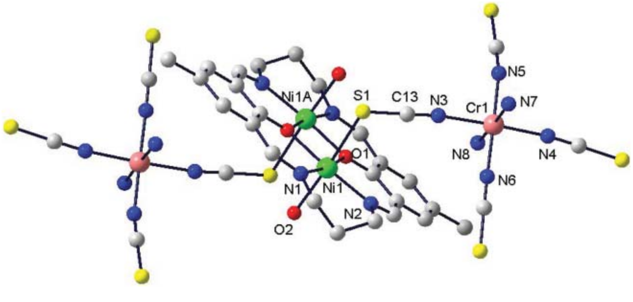


Fig. 5 View of the [CrNiNiCr] tetranuclear complex **4**.

Heterometallic systems constructed from 3d–3d′ nodes

The main interest in heterometallic complexes arises from their magnetic properties. The combination of metal ions carrying different spins is an important chapter in modern molecular magnetism.[17] The classical synthetic approach toward heterometallic complexes consists of self-assembly processes between anionic complexes acting as ligands and assembling cations (Scheme 2).[18] We have developed an alternative way to obtain heterospin systems, by connecting preformed heterometallic nodes with various ligands (Scheme 3). The intra-node

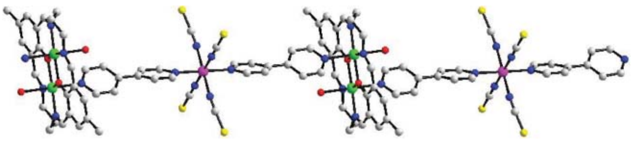
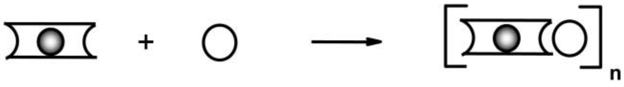
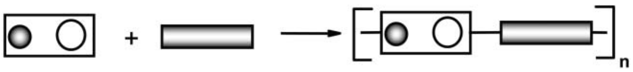


Fig. 6 A cationic heterometallic chain in compound **5**. Colour code: Cr – pink; Ni – green; O – red; N – blue; S – yellow.



Scheme 2



Scheme 3

exchange interactions, as well as those between the resulting spins, can generate interesting magnetic properties. A rich library of discrete heterometallic complexes, which can act as nodes, is available.[19] We have chosen as tectons complexes with compartmental dissymmetric Schiff-base ligands (**IV**, **V**, **VI**). These ligands are readily accessible and allow good control over the number and the nature of the metal ions.

Complexes of type **IV** are obtained through the stepwise template condensation of 2,6-diformyl-*p*-cresol with ethylenediamine and diethylenetriamine.[20] All of them contain $\mathrm{Cu^{II}}$ and another transition metal ion. Since the second metal(II) ion has only one accessible coordination site, the other five being occupied by three nitrogen atoms and two phenoxo oxygens, these complexes generate mainly discrete polymetallic systems. The hexanuclear complex, $[\{\mathrm{MnCuL}\}_3(\mathrm{TMA})](\mathrm{ClO_4})_3\cdot 8\mathrm{H_2O}$ **6**, has been obtained by connecting three heterobinuclear $[\mathrm{LCu^{II}Mn^{II}}]^{2+}$ species through the anion of the trimesic acid ($\mathrm{L^{2-}}$ is the above mentioned macrocyclic compartmental ligand).[21] The trimesate anion has been chosen not only because of its potential ability to connect 3 × 2 metal ions, but also since it fulfils the necessary conditions to mediate a ferromagnetic coupling through a spin polarization mechanism: the whole bridging molecule can be planar, and the metallic centres are separated by an odd number of atoms. Although predicted, this ability of the trimesate anion has never been observed with other complexes. Complex **6** exhibits a C_3 rotational symmetry imposed by the geometry of the linker (Fig. 7). The $\mathrm{Mn^{II}}$ and $\mathrm{Cu^{II}}$ ions within each pair are bridged by two phenoxo oxygen atoms and by a carboxylato group arising from the $\mathrm{TMA^{3-}}$ spacer. The magnetic properties of compound **6** are in line with our expectations. On lowering the temperature, the $\chi_{\mathrm{M}}T$ product decreases continuously, reaching a minimum at 12 K ($\mathrm{Cu^{II}}$–$\mathrm{Mn^{II}}$ intra-node antiferromagnetic interaction, with $J_1 = -16.7\ \mathrm{cm^{-1}}$), then increases (ferromagnetic coupling among the three resulting $S = 2$ spin units through the spin polarization mechanism, $J_2 = +0.05\ \mathrm{cm^{-1}}$) (Fig. 8).

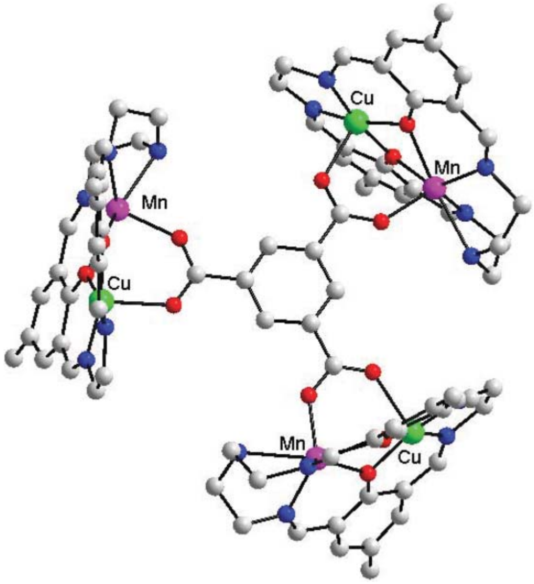


Fig. 7 Perspective view of the $[\mathrm{Mn_3Cu_3}]^{3+}$ hexanuclear ion in compound **6**.

The reaction of the [CuZn] derivative with bis(4-pyridyl)ethylene affords a molecular rectangle: $[(\mathrm{CuZnL})_2(\mathrm{bpete})_2](\mathrm{ClO_4})_4\cdot 4.5\mathrm{CH_3OH}$ **7** (Fig. 9),[11c] with the following dimensions: short sides 3.198 Å, long sides 13.69 Å.

In order to obtain $\mathrm{Cu^{II}}$–$\mathrm{M^{II}}$ coordination polymers, the compartment accommodating the second metal ion must be more flexible, allowing the access of more than one bridging ligand. Nodes of type **V** can be obtained by reacting the mononuclear copper(II) complex (copper ion hosted into the $\mathrm{N_2O_2}$ compartment) with a second metal ion. A $\mathrm{Cu^{II}Co^{II}}$ coordination polymer, $^{1}_{\infty}[\mathrm{LCu^{II}Co^{II}(NCS)_2}]$ **8**, was obtained by reacting the [CuL] mononuclear complex with cobalt(II) acetate and KSCN ($\mathrm{L^{2-}}$ is the ligand obtained by reacting 3-methoxysalicylaldehyde with propylenediamine).[22] Its crystal structure consists of zigzag chains made up of alternating

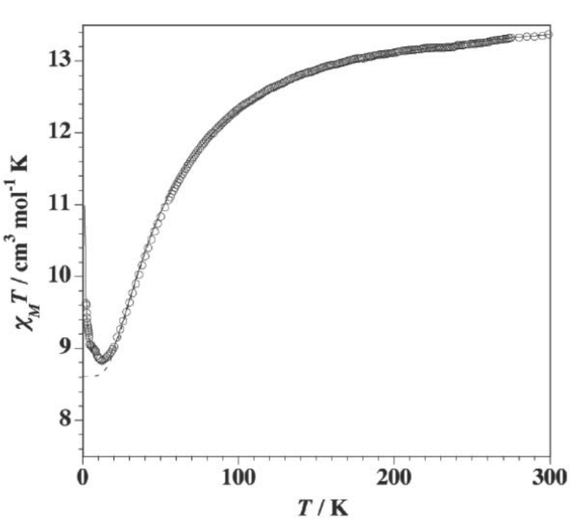


Fig. 8 Diagram showing the temperature variation of the $\chi_{\mathrm{M}}T$ product for compound **6**.

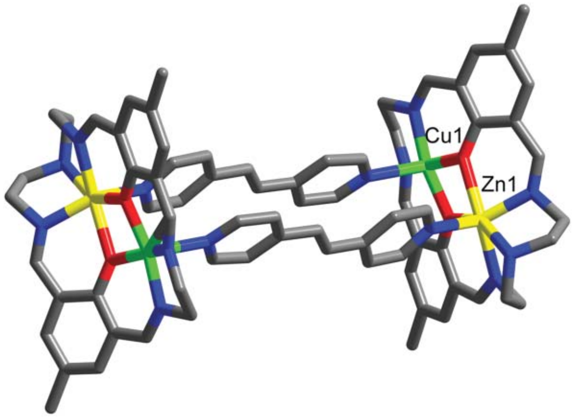
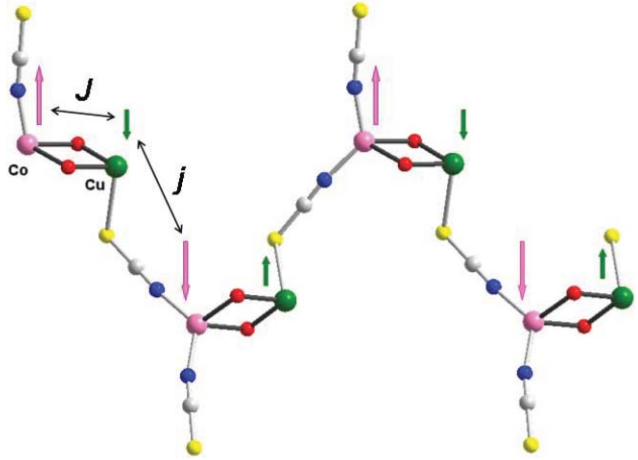


Fig. 9 Illustration of a cationic rectangle, $[(CuZnL)_2(bpete)_2]^{2+}$, in compound **7**.



Scheme 4

up and down dinuclear {LCuCo} units linked by thiocyanato bridges (Fig. 10). The intra-node Cu···Co distance is 3.149(1) Å, while the Cu···Co distance for the NCS^- bridged ions is equal to 6.125(1) Å. The cobalt(II) ions display a strongly distorted [4 + 2] octahedral geometry. The magnetic properties of **8** will depend on two parameters related to the Cu–Co exchange interactions supported by the two phenoxo bridges (intranode, J_1), and by the thiocyanato bridge (J_2). The best fit to the magnetic data takes into account the zero field splitting parameter associated with Co^{II}, D, and leads to the following values: $J_1 = -101.2$ cm^{-1}, $J_2 = +2.8$ cm^{-1}, $D = -0.11$ cm^{-1}. The large antiferromagnetic interaction, J_1, is attributed to the double bridge Cu(O,O)Co pathway, and the ferromagnetic term, J_2, to the Co–NCS–Cu one. The internode ferromagnetic interaction is not surprising, since the dinuclear (Cu,Co) entities are alternately disposed up and down, so that the spins of the cobalt and copper ions located at the two ends of the NCS bridge are oriented in a parallel direction (Scheme 4).

The heterotopic bicompartmental ligands are suited for designing heterobimetallic complexes. The archetype can be considered the family of Schiff-bases derived from 3-formylsalicylic acid.[23] We developed a new synthetic method for tetranuclear heterometal complexes relying upon bis(bicompartmental) ligands. One ligand of this type results from the reaction of 3-formylsalicylic acid with hydrazine. This diazine acts also as a helicand that generates heterometallic tetranuclear helicates. The helicate itself can act as a ligand toward a third metal ion, through the peripheral oxygen atoms arising from the carboxylato groups. The reaction between the tetratopic diazine and cobalt(II) perchlorate, iron(III) perchlorate, and sodium carbonate leads to triple stranded tetranuclear anionic helicates, $[L_3Co^{II}_2Fe^{III}_2]^{2-}$, which are connected through sodium ions, resulting in chiral coordination polymers, $^1_\infty[L_3Na_2Fe_2Co_2(H_2O)_4(EtOH)_2]\cdot 3H_2O$ **9** (Fig. 11).[24] Heterometallic complexes of this type, that is, helicates constructed from pairs of antiferromagnetically coupled metal ions with a non-zero resulting spin, are very good candidates to emphasize interesting magnetic properties (for example, the occurrence of spin canting in isolated species). In the case of compound **9** the $\{Fe^{III}–Co^{II}\}$ pairs connected by $\mu_{1,2}$ diazino-bridges are related by a binary axis. Therefore the easy axes of each cobalt ion are pointing in different directions and the coupling of the $\{Fe^{III}–Co^{II}\}$ pairs leads to a sort of weak ferromagnetism.[24]

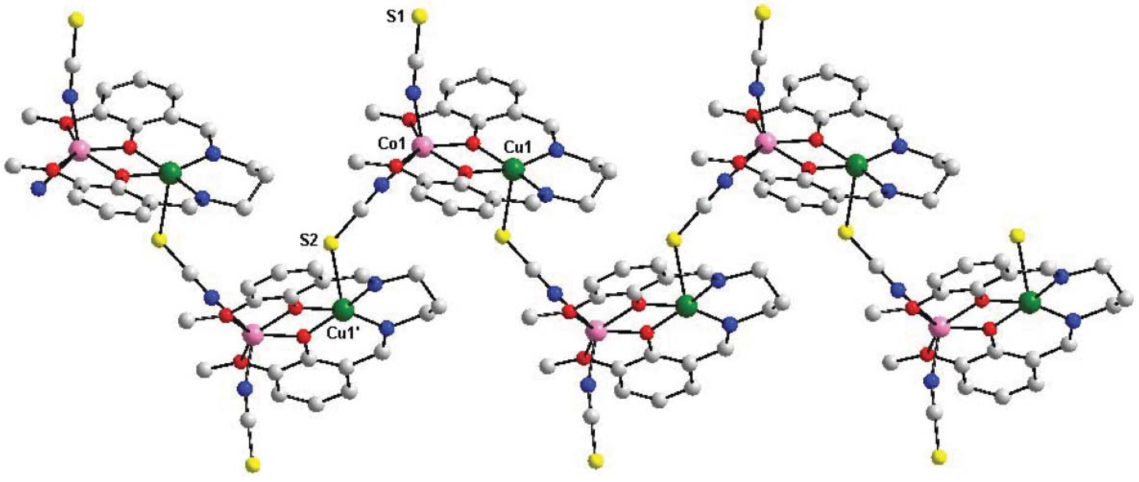


Fig. 10 Crystal structure of $^1_\infty[LCu^{II}Co^{II}(NCS)_2]$ **8**.

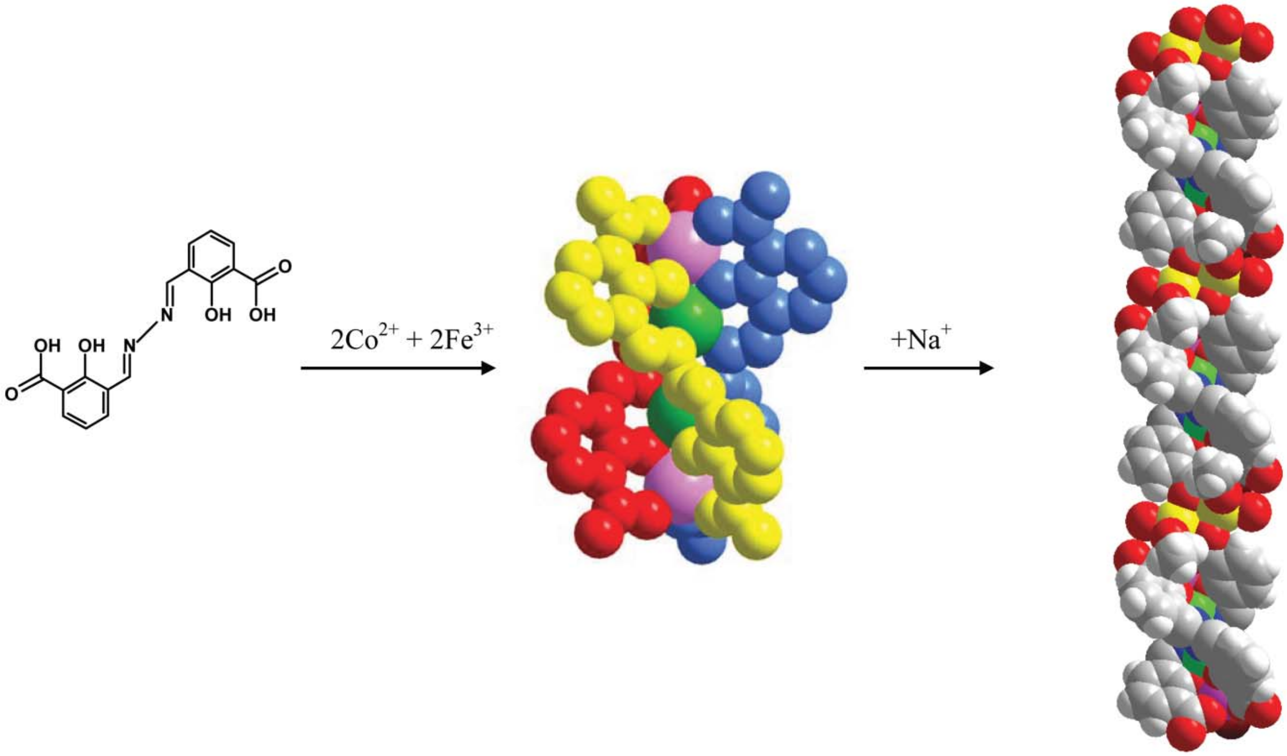


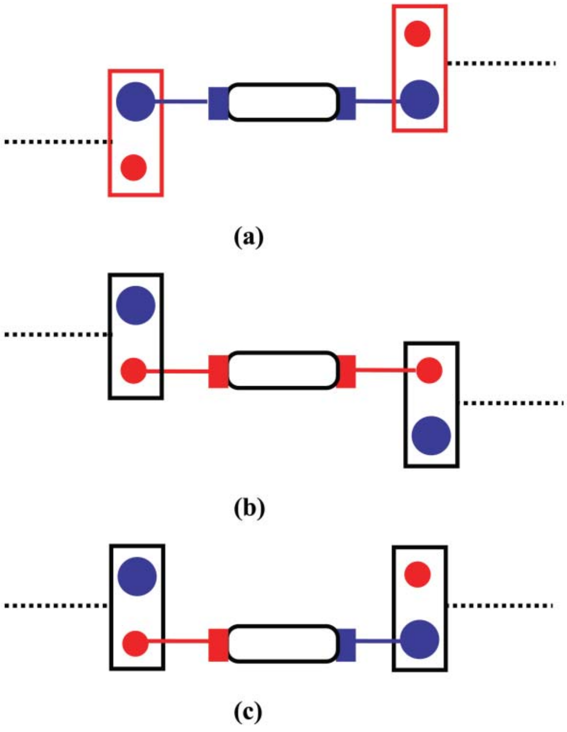
Fig. 11 Formation of the heterometallic triple stranded helicate, **9**. Colour code: Fe – pink; Co – green; Na – yellow.

Heterometallic systems constructed from 3d–4f nodes

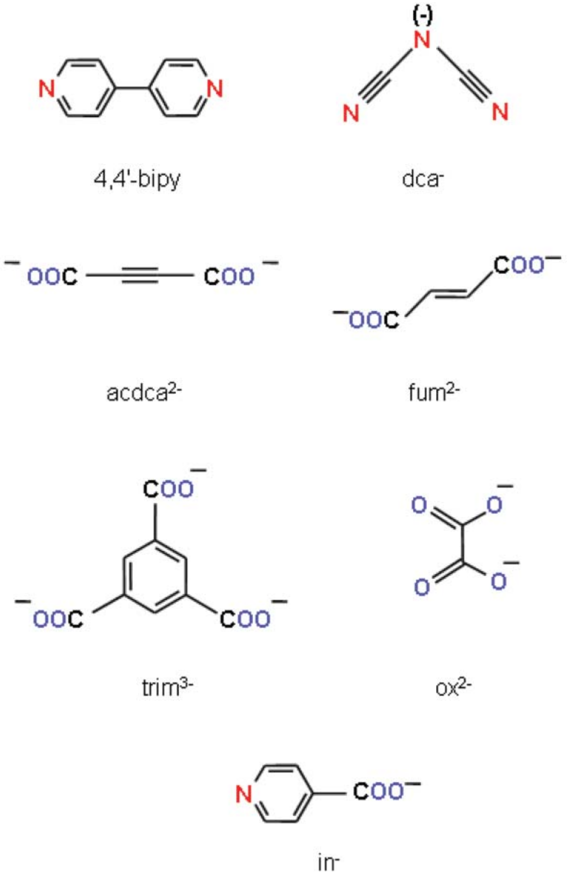
The compartmental ligands derived from 3-methoxysalicylaldehyde and a diamine, **VI**, have been specially designed to give binuclear 3d–4f complexes.[25] Their exceptional versatility as building blocks is due to the presence of two metal ions which differ drastically in their chemical behaviour: the rare earth cations are hard acids, with a strong oxophilic character and high coordination numbers, whereas copper(II) is a borderline acid with a marked tendency to adopt a more or less distorted square-pyramidal geometry. Consequently, they can interact selectively with various spacers (Scheme 5: red–red = copper–nitrogen interaction; blue–blue = lanthanide–oxygen interaction).[26]

Three families of linkers were employed (Schemes 5 and 6): (a) *exo*-dentate ligands bearing nitrogen donor atoms; (b) *exo*-dentate ligands with oxygen donor atoms; (c) *exo*-dentate ligands bearing both nitrogen and oxygen donor atoms. The ligands belonging to the first family are supposed to interact preferentially with the copper(II) ions. On the other hand, we anticipate that the ligands from the second family will prefer the oxophilic rare earth cations. Finally, the isonicotinic acid is expected to interact through the nitrogen atom with the copper ion, and through the oxygen atoms with the rare earth cation.

As expected, when reacting $[LCu^{II}Gd^{III}(NO_3)_3]$ and 4,4′-bipy, the spacer interacts only with the copper(II) ions, linking two [GdCu] units (H_2L is the Schiff-base resulting from the 2 : 1 condensation of 3-methoxysalicylaldehyde with propylenediamine). A tetranuclear complex, $[\{LCu^{II}Gd^{III}(NO_3)_3\}_2(\mu\text{-}4,4'\text{-bipy})]$ **10**, is formed (Fig. 12). Conversely, the interaction of the $[LCuGd]^{3+}$ cation with the dianion of acetylenedicarboxylic acid, $acdca^{2-}$, affords a 1-D coordination polymer, $^{1}_{\infty}[LCu^{II}Gd^{III}(acdca)_{1.5}(H_2O)_2]\cdot 13H_2O$ **11**, in which the spacer interacts only with the gadolinium ions (Fig. 13). The


(a)
(b)
(c)

Scheme 5



Scheme 6

{LCuGd} entities are alternately bridged by one and two dicarboxylato ligands having different connectivity modes: with the single bridge, the acetylenedicarboxylato ligand acts as bis-chelating ligand towards two gadolinium ions, while with the double bridge each carboxylato group acts as unidentate ligand.

Three different types of coordination polymers were obtained by using fumaric acid, H_2fum: ${}^{2}_{\infty}[\mathrm{LCu^{II}Gd^{III}(fum)_{1.5}(H_2O)_2}]\cdot 4\mathrm{H_2O}\cdot \mathrm{C_2H_5OH}$ **12**, ${}^{1}_{\infty}[\mathrm{LCu^{II}Sm^{III}(H_2O)(Hfum)(fum)}]$ **13**, and ${}^{1}_{\infty}[\mathrm{LCu^{II}Er^{III}(H_2O)_2(fum)}](\mathrm{NO_3})\cdot 3\mathrm{H_2O}$ **14**. None of these structures is similar to **11**. The gadolinium derivative, **12**, is a 2-D coordination polymer, the samarium one, **13**, is a double chain, while the erbium derivative, **14**, is a single chain. Compound **12** has the same stoichiometry as the 1-D acetylenedicarboxylato derivative, **11**, excepting the crystallization solvent molecules, but its structure is completely different: **12** is a two-dimensional coordination polymer with a brick wall architecture (Fig. 14a). Each {CuGd} entity is connected through fumarato bridges to three other heterobinuclear units. Two out of the three fumarato linkers connect the gadolinium ions from three {CuGd} units, with each carboxylato group acting as a chelator. For the third fumarato linker, each carboxylato group bridges the $\mathrm{Cu^{II}}$ and $\mathrm{Gd^{III}}$ ions within the {CuGd} building block (*syn–syn* bridging mode).

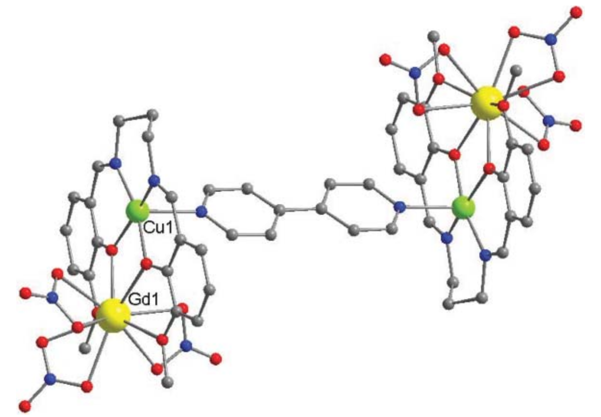


Fig. 12 The tetranuclear complex **10** obtained by connecting two [CuGd] binuclear nodes with 4,4′-bipyridine.

The {CuSm}–fumaric acid system is quite interesting. The above mentioned dicarboxylato complexes, **11** and **12**, were obtained by reacting the {CuGd} precursors with the corresponding dicarboxylates. By reacting the {CuSm} precursor only with fumaric acid, ${}^{1}_{\infty}[\mathrm{LCu^{II}Sm^{III}(H_2O)(Hfum)(fum)}]$ **13** is obtained. One of the fumaric acid molecules is fully deprotonated, while the other one is monodeprotonated. The fum^{2-} and Hfum^{-} species are coordinated only to the samarium ions: the first one acts as a bridge, while the second one is a terminal ligand, with the chelating carboxylato group coordinated to samarium (Fig. 14b). The complete deprotonation of the fumaric acid leads to ${}^{2}_{\infty}[\mathrm{LCu^{II}Sm^{III}(fum)_{1.5}(H_2O)_2}]\cdot 4\mathrm{H_2O}\cdot \mathrm{C_2H_5OH}$, which is isomorphous with **12**.

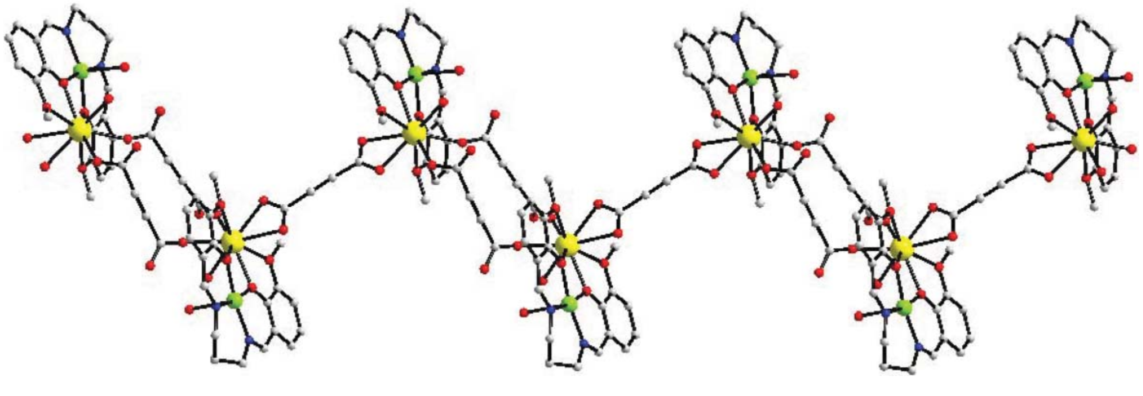
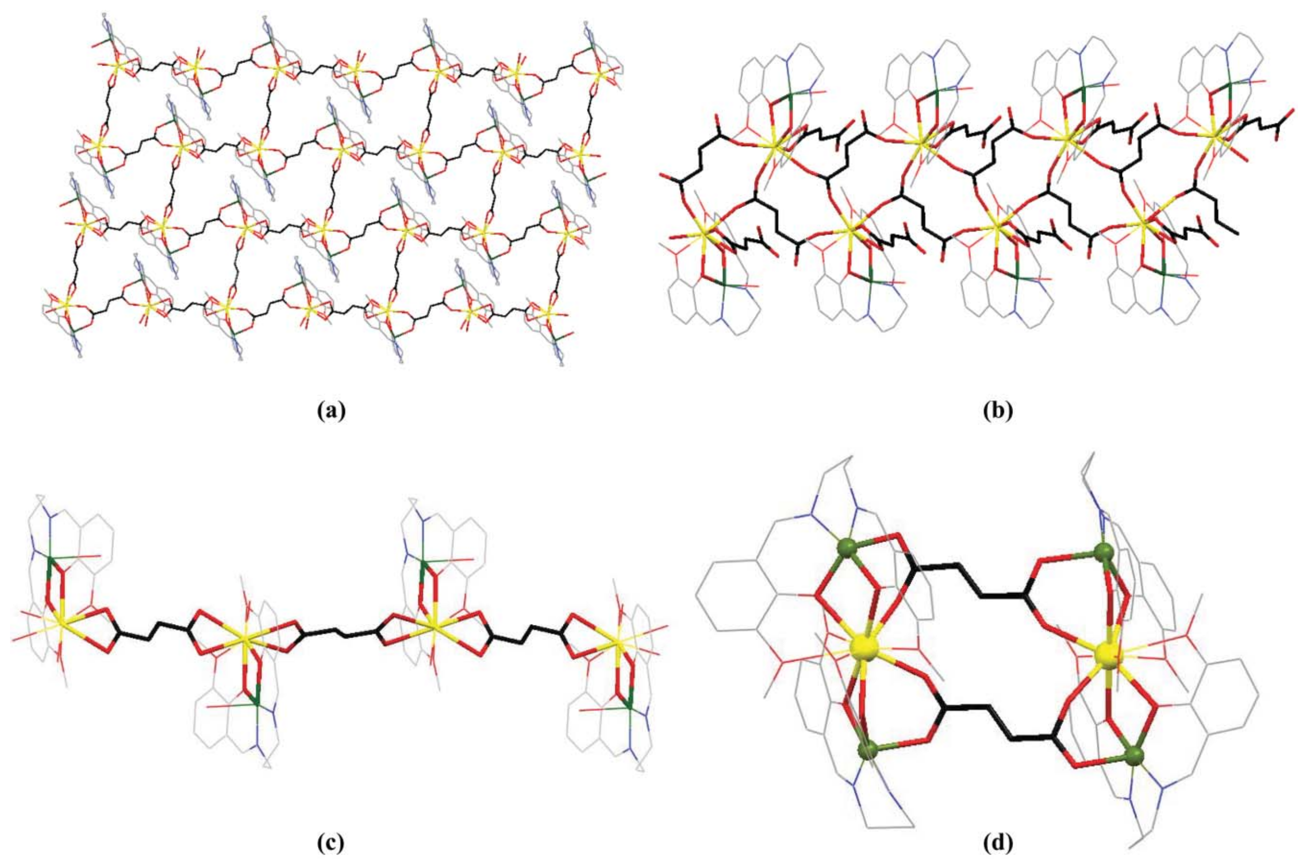


Fig. 13 Illustration of a 1-D coordination polymer **11** obtained by connecting [CuGd] nodes with the dianion of acetylenedicarboxylic acid.



(a) (b) (c) (d)

Fig. 14 Coordination polymers obtained by using the anions of fumaric acid as spacers: (a) $^{2}_{\infty}[LCu^{II}Gd^{III}(fum)_{1.5}(H_2O)_2]\cdot 4H_2O\cdot C_2H_5OH$ **12** (2-D); (b) $^{1}_{\infty}[LCu^{II}Sm^{III}(H_2O)(Hfum)(fum)]$ **13** (1-D, double chain); (c) $^{1}_{\infty}[LCu^{II}Er^{III}(H_2O)_2(fum)](NO_3)\cdot 3H_2O$ **14** (1-D, single chain); (d) $[\{(LCu^{II})_2Sm^{III}\}_2fum_2](OH)_2$ **15** (hexanuclear).

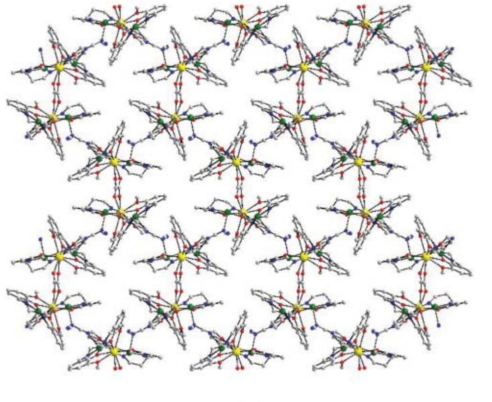
The reaction between the erbium derivative, $[LCuEr(NO_3)_3]$, fumaric acid and LiOH (molar ratio [CuEr] : fumaric acid = 1 : 1) leads to a different compound: $^{1}_{\infty}[LCu^{II}Er^{III}(H_2O)_2(fum)](NO_3)\cdot 3H_2O$ **14**. In this case, only two out of the three nitrato ligands were replaced by one fumarato dianion. It results in a one-dimensional coordination polymer with the {CuEr} nodes connected by fum^{2-} bridges. The carboxylato groups are coordinated only to the erbium ions (chelating) – Fig. 14c.

The investigation of the magnetic properties of complexes **10**, **11**, **12** reveals a ferromagnetic intranode Cu^{II}–Gd^{III} interaction with, respectively, the following J values: 8.96; 5.98; 3.53 cm^{-1} ($\boldsymbol{H} = -J\boldsymbol{S}_1\boldsymbol{S}_2$).[26a]

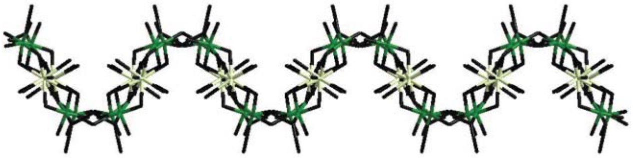
[CuLn] binuclear complexes were obtained by reacting the mononuclear copper(II) complex with a Ln^{III} salt in a 1 : 1 molar ratio. It has been observed that trinuclear [CuLnCu] species can be assembled as well.[27] By reacting the mononuclear Schiff-base copper(II) complex with samarium nitrate and fumaric acid in a 2 : 1 : 1 molar ratio (in the presence of LiOH), a hexanuclear complex based upon the $[Cu_2Sm]$ entity was formed: $[\{(LCu^{II})_2Sm^{III}\}_2fum_2](OH)_2$ **15** (Fig. 14d). The two $\{Cu_2Sm\}$ moieties are linked through two fum^{2-} ions. Each carboxylato group acts as a bridge between the copper and samarium ions (the classical *syn–syn* bridging mode). A similar $[Zn_4Nd_2]$ hexanuclear complex cation has been obtained recently by using the same compartmental ligand and 1,4-benzenedicarboxylato as a linker.[28] This compound exhibits NIR luminescence both in solution and the solid state.

Taking into account the preference of the copper(II) ions for the nitrogen atoms, and the one of the lanthanide ions for the oxygen atoms, we used two different bridging ligands: dicyanamido, dca^{-}, with only nitrogen donor atoms, and the other one with only oxygen donor atoms (oxalato, ox^{2-}). The self-assembly process between $[(LCu)_2Pr]^{3+}$ complex ions, dicyanamido and oxalato ions leads to a quite interesting compound: $^{2}_{\infty}[\{(LCu)_2Pr\}(C_2O_4)_{0.5}(dca)](dca)\cdot 2H_2O$ **16** (Fig. 15), whose structure can be easily rationalized, since it is based on the selective interaction of the metallic centres with the bridging ligands. The cationic 2-D coordination polymer in **16** is built up of almost linear trinuclear $[Cu_2Pr]$ entities, which are connected by dicyanamido and oxalato ligands. The praseodymium ions from two trinuclear units are bridged by an oxalato ligand, resulting in hexanuclear moieties. These are further interconnected through 1,3-dicyanamido linkers, which coordinate to the copper ions, as illustrated in Scheme 7, resulting in corrugated sheets (Fig. 15b).

A 2-D coordination polymer, $^{2}_{\infty}[LCu^{II}Pr^{III}(NO_3)_2(in)]$ **17**, has been obtained by employing the isonicotinate ion, in^{-}, as a linker with two different coordination sites. The heterobinuclear units, $[LCuPr(NO_3)_2]^{+}$, are connected through the unsymmetrical *exo*-bidentate ligands, leading to an extended structure (Fig. 16). The building principle is based on the



(a)



(b)

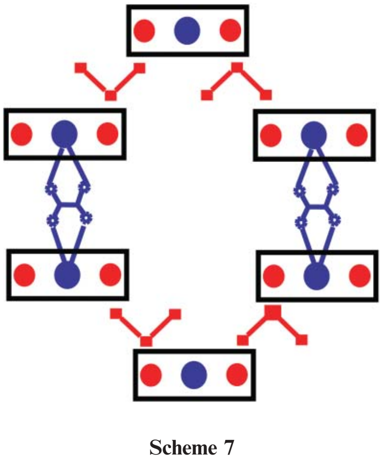
Fig. 15 Formation of corrugated cationic layers in **16** by connecting [Cu_2Pr] nodes through oxalato and dicyanamido bridges: (a) top view; (b) side view.

selective interaction of the spacer, in^-, which coordinates with the carboxylato group to the oxophilic Pr^{III} ions and, with the nitrogen atom, to the Cu^{II} ion (Scheme 8).

Two other 1-D coordination polymers were constructed from [CuGd] nodes and thiocyanato or dicyanamido linkers.[29] The intranode coupling is ferromagnetic, while the interaction between the nodes was found to be extremely weak antiferromagnetic.

Polynuclear complexes with three different spin carriers: 3d–3d′–4f and 2p–3d–4f systems

The synthetic approach based upon 3d–4f tectons can be extended towards the construction of coordination polymers containing three different spin carriers: 3d–3d′–4f, 2p–3d–4f, 3d–4d–4f, *etc*. The resulting compounds are of high interest in molecular magnetism, providing both physicists and theoreticians with exciting cases for investigation. The third spin carrier could add new properties/functions to the magnetic material. The [$LCuLn(NO_3)_3$] complexes are again suitable precursors: the nitrato ligands can be replaced by connectors carrying the third spin carrier, for example hexacyano complex anions, $[M(CN)_6]^{3-}$ (M = Cr, Fe, Co). A family of isomorphous heterotrimetallic chains, $[\{LCu\}Ln(H_2O)_3\{M(CN)_6\}]\cdot 4H_2O$ **18**, has been obtained.[26a,30] The



Scheme 7

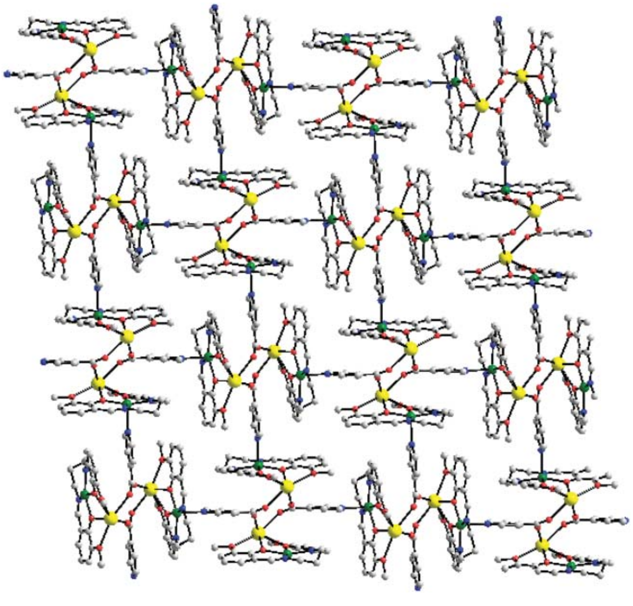
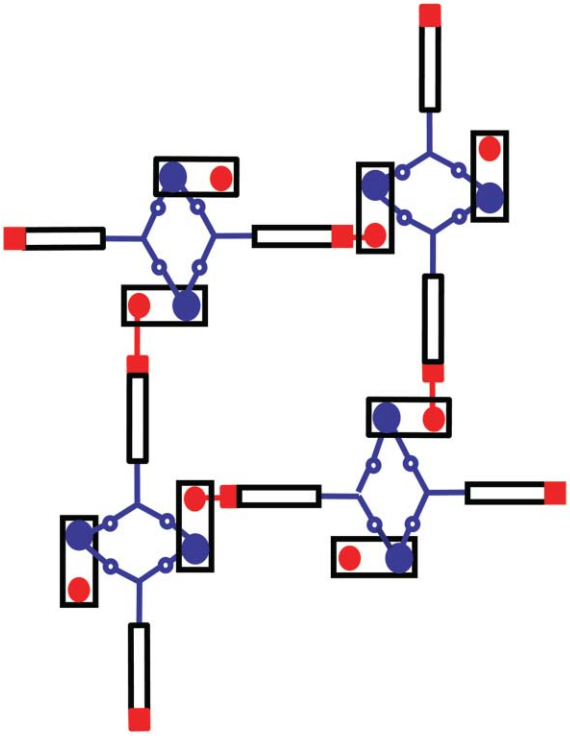


Fig. 16 View of the 2-D coordination polymer, **17**, obtained by connecting [CuPr] nodes with the isonicotinato anion.



Scheme 8

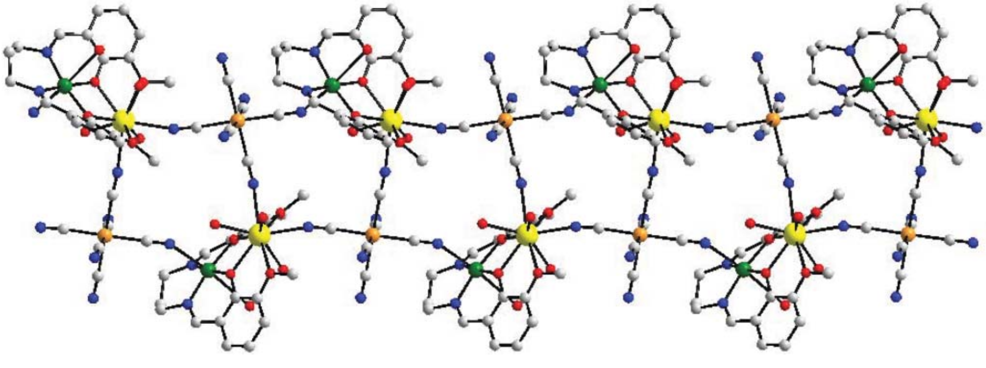


Fig. 17 Perspective view of the 3d–3d′–4f coordination polymers, **18**, obtained by reacting $[LCuLn(NO_3)_3]$ complexes with $[M(CN)_6]^{3-}$ ions.

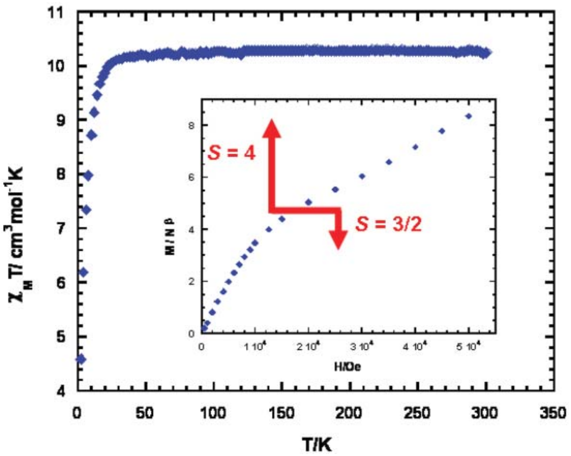


Fig. 18 Magnetic properties of $[\{LCu\}Ln(H_2O)_3\{Cr(CN)_6\}]\cdot 4H_2O$: $\chi_M T$ *vs.* T curve; inset: the magnetization *vs.* field curve.

$[M(CN)_6]^{3-}$ ion connects three metal ions (two Cu^{II} and one Ln^{III}), through three meridially disposed cyano groups, resulting in a ladder-type topology (Fig. 17). The $[Cu^{II}Gd^{III}Co^{III}]$ derivative gives information on the [CuGd] interaction within the whole $[Cu^{II}Gd^{III}M^{III}]$ family (J_{CuGd} = 7.24 cm^{-1}). The magnetic behaviour of the $[Cu^{II}Gd^{III}Cr^{III}]$ and $[Cu^{II}Gd^{III}Fe^{III}]$ derivatives results from the combination of the following exchange interactions: Cu^{II}–Gd^{III} (ferro) and Gd^{III}–M^{III} (antiferro). The intranode ferromagnetic Cu^{II}–Gd^{III} interaction is overwhelmed by the Gd^{III}–Cr^{III} antiferromagnetic interactions (Fig. 18). The antiferromagnetic coupling between the {CuGd} nodes and the $[Cr(CN)_6]^{3-}$ units is clearly indicated by the magnetization *versus* field measurements (inset Fig. 18). At low fields, the magnetization has a regular increase, then undergoes an inflexion point (*ca.* 5 Nβ at 2.0 kG), and increases linearly. The inflexion point corresponds to a spin S = 5/2, resulting from the antiferromagnetic interaction between the nodes (S = 4) and the chromium(III) ions (S = 3/2). Several other 3d–3d′–4f systems with interesting magnetic properties were reported recently.[31]

The first $2p(TCNQ^{\bullet -})$–$3d(Cu^{2+})$–$4f(Gd^{3+})$ heterospin complex, $[\{CuL\}_2Gd(TCNQ)_2]\cdot(TCNQ)\cdot(CH_3OH)\cdot 2CH_3CN$ **19**, has been obtained by reacting the mononuclear precursor, [CuL], with gadolinium nitrate and LiTCNQ.[32] Its structure consists of almost linear trinuclear $[Cu_2Gd]$ units on which $TCNQ^{\bullet -}$ anionic radicals are attached. The $TCNQ^{\bullet -}$ ions are involved in both coordinative and stacking interactions. One $TCNQ^{\bullet -}$ radical is coordinated to the gadolinium atom, which achieves a coordination number of nine. The second $TCNQ^{\bullet -}$ acts as a bridging ligand between copper(II) ions from neighbouring $[Cu_2Gd]$ units, resulting in infinite chains (Fig. 19). The third $TCNQ^{\bullet -}$ ion is uncoordinated. The stacked $TCNQ^{\bullet -}$ ions do not contribute to the magnetic moment of **19** because of their strong antiferromagnetic coupling.

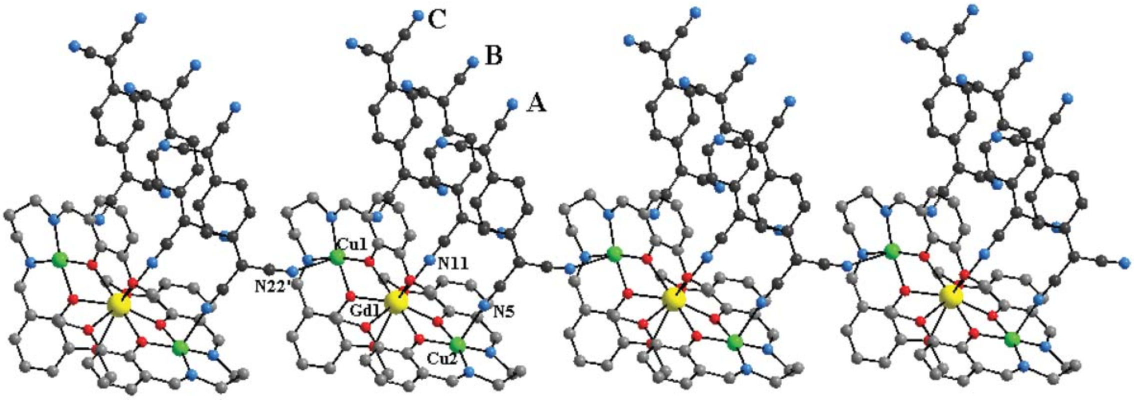


Fig. 19 View of the 2p–3d–4f coordination polymer, **19**. There are three types of $TCNQ^{\bullet -}$ anions: **A** – bridging the copper ions from two [Cu2Gd] nodes; **B** – coordinated to gadolinium; **C** – uncoordinated.

Conclusion and outlook

The development of crystal engineering continuously needs new tectons and new connectivity rules to be applied in order to obtain the desired network topologies. The examples presented herein illustrate that preformed oligonuclear complexes act efficiently as building blocks in designing heterometallic 1-D, 2-D or 3-D coordination polymers, as well as high-nuclearity clusters. We focused mainly on the following tectons: (a) bis(alkoxo)-bridged copper(II) species; (b) homobinuclear species with metal ions held together by end-off, or macrocyclic compartmental ligands; (c) heterometallic complexes with dissymmetric compartmental ligands. Their versatility increases when the metal ions differ drastically in their chemical behaviour. This is the case for the 3d–4f oligonuclear complexes. Many other oligonuclear complexes of these types can be designed or merely found in the literature.

We have shown that the spacers mediate antiferromagnetic or, more interestingly, ferromagnetic interactions between the spins resulting from the intranode magnetic coupling. Interesting magnetic properties are expected when the spacer itself is paramagnetic. The combination of three different spin carriers could lead to a new generation of molecule-based magnetic materials especially when the metal ions are strongly anisotropic (as a prerequisite for obtaining single molecule magnets or single chain magnets). New multifunctional materials can be obtained as well, if the third spin carrier (*e.g.* paramagnetic complexes with dithiolene ligands) is involved in conducting phases.

The use of chiral spacers connecting multimetallic nodes remains largely unexploited and can open new perspectives in both crystal engineering and molecular magnetism. Exciting magnetic materials are expected when the magnetic clusters are connected by photoactive spacers (*e.g.* $[Mo(CN)_8]^{4-}$ ions).

Acknowledgements

I would like to express my gratitude to all my coworkers, colleagues and students. Their names appear in the references listed. Financial support from the CEEX (Project D11-17) and CERES (Project 4/130) Programmes, as well as EC "MAGMANet" NMP3-CT-2005-515767 is gratefully acknowledged.

Notes and references

1 (*a*) E. C. Constable, *Pure Appl. Chem.*, 1996, **68**, 253; (*b*) E. C. Constable, in *Comprehensive Supramolecular Chemistry*, ed. J.-M. Lehn, L. Atwood, J. E. D. Davis, D. D. MacNicol and F. Vögtle, Pergamon, Oxford, 1996, Vol. 9, p. 213.

2 (*a*) N. R. Champness, *Dalton Trans.*, 2006, 877; (*b*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629; (*c*) J. D. Wuest, *Chem. Commun.*, 2005, 5830; (*d*) K. Biradha, M. Sarkar and L. Rajput, *Chem. Commun.*, 2006, 4169; (*e*) Y. Zhou, M. Hong and X. Wu, *Chem. Commun.*, 2006, 135.

3 (*a*) O. Kahn, *Acc. Chem. Res.*, 2000, **33**, 647; (*b*) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; (*c*) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; (*d*) C. J. Kepert, *Chem. Commun.*, 2006, 695; (*e*) S. Kitagawa, S. Noro and T. Nakamura, *Chem. Commun.*, 2006, 701; (*f*) O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511; (*g*) E. Coronado and J.-R. Galán-Mascarós, *J. Mater. Chem.*, 2005, **15**, 66; (*h*) D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Prior and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273.

4 (*a*) R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 1677; (*b*) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546.

5 (*a*) J.-M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Germany, 1995; (*b*) J.-M. Lehn, *Science*, 2002, **295**, 2400.

6 F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759 and references therein.

7 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.

8 H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276.

9 M. A. S. Aquino, *Coord. Chem. Rev.*, 2004, **248**, 1025 and references therein.

10 See for example: (*a*) Y. Liao, W. W. Shum and J. S. Miller, *J. Am. Chem. Soc.*, 2002, **124**, 9337; (*b*) T. E. Vos, Y. Liao, W. W. Shum, J.-H. Her, P. W. Stephens, W. M. Reiff and J. S. Miller, *J. Am. Chem. Soc.*, 2004, **126**, 11630.

11 See for example: (*a*) W. Huang, S. Gou, D. Hu, S. Chantrapromma, H.-K. Fun and Q. Meng, *Inorg. Chem.*, 2001, **40**, 1712; (*b*) A. Asokan, B. Varaghese, A. Caneschi and P. T. Manoharan, *Inorg. Chem.*, 1098, **37**, 228; (*c*) M. Pascu, M. Andruh, A. Müller and M. Schmidtmann, *Polyhedron*, 2004, **23**, 673; (*d*) G. S. Papaefstathiou, I. G. Georgiev and L. R. MacGillivray, *Chem. Commun.*, 2005, 673.

12 M. Andruh, *Pure Appl. Chem.*, 2005, **77**, 1685.

13 See, for example: (*a*) M. J. Katz, C. J. Shorrock, R. J. Batchelor and D. B. Leznoff, *Inorg. Chem.*, 2006, **45**, 1757; (*b*) G. Marin, V. Tudor, V. Ch. Kravtsov, M. Schmidtmann, Y. A. Simonov, A. Müller and M. Andruh, *Cryst. Growth Des.*, 2005, **5**, 279; (*c*) V. Tudor, V. Kravtsov, Y. A. Simonov, J. Lipkowski and M. Brezeanu, *Inorg. Chim. Acta*, 2003, **353**, 35.

14 C. Paraschiv, M. Andruh, S. Ferlay, M. Wais Hosseini, N. Kyritsakas, J.-M. Planeix and N. Stanica, *Dalton Trans.*, 2005, 1195.

15 See, for example: L. Schwabe and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1985, 1909 and references therein.

16 (*a*) L. Toma, L. M. Toma, R. Lescouëzec, D. Armentano, G. De Munno, M. Andruh, J. Cano, F. Lloret and M. Julve, *Dalton Trans.*, 2005, 1357; (*b*) A. Cucos, N. Avarvari, M. Andruh, Y. Journaux, A. Müller and M. Schmidtmann, *Eur. J. Inorg. Chem.*, 2006, 903.

17 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.

18 (*a*) O. Kahn, *Adv. Inorg. Chem.*, 1995, **43**, 179; (*b*) R. Ruiz, J. Faus, F. Lloret, M. Julve and Y. Journaux, *Coord. Chem. Rev.*, 1999, **193–195**, 1069; (*c*) 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 and F. Villain, *Coord. Chem. Rev.*, 1999, **190–192**, 1023; (*d*) M. Ohba and H. Okawa, *Coord. Chem. Rev.*, 2000, **198**, 313; (*e*) R. Lescouëzec, L. M. Toma, J. Vaissermann, M. Verdaguer, F. S. Delgado, C. Ruiz-Pérez, F. Lloret and M. Julve, *Coord. Chem. Rev.*, 2005, **249**, 2691.

19 See, for example: (*a*) P. A. Vigato and S. Tamburini, *Coord. Chem. Rev.*, 2004, **248**, 1717 (Schiff-base polynuclear complexes); (*b*) A. L. Gavrilova and B. Bosnich, *Chem. Rev.*, 2004, **104**, 349 (Binucleating ligands); (*c*) M. Sakamoto, K. Manseki and H. Okawa, *Coord. Chem. Rev.*, 2001, **219–221**, 379 (3d–4f complexes); (*d*) A. J. Atkins, D. Black, A. J. Blake, A. Marin-Becerra, S. Parsons, L. Ruiz-Ramirez and M. Schröder, *Chem. Commun.*, 1996, 457; (*e*) H. Okawa, H. Furutachi and D. E. Fenton, *Coord. Chem. Rev.*, 1998, **175**, 51 (Compartmental ligands).

20 H. Okawa, J. Nishio, M. Ohba, M. Tadakoro, N. Matsumoto, M. Koikawa, S. Kida and D. E. Fenton, *Inorg. Chem.*, 1993, **32**, 2949.

21 M. Pascu, F. Lloret, N. Avarvari, M. Julve and M. Andruh, *Inorg. Chem.*, 2004, **43**, 5189.

22 J.-P. Costes, R. Gheorghe, M. Andruh, S. Shova and J.-M. Clemente Juan, *New J. Chem.*, 2006, **30**, 572.

23 O. Kahn, *Struct. Bonding*, 1987, **68**, 89.

24 P. Cucos, M. Pascu, R. Sessoli, N. Avarvari, F. Pointillart and M. Andruh, *Inorg. Chem.*, 2006, **45**, 7035.

25 J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Inorg. Chem.*, 1996, **35**, 2400.

26 (*a*) R. Gheorghe, P. Cucos, M. Andruh, J.-P. Costes, B. Donnadieu and S. Shova, *Chem.–Eur. J.*, 2006, **12**, 187; (*b*) R. Gheorghe, M. Andruh, A. Müller and M. Schmidtmann, *Inorg. Chem.*, 2002, **41**, 5314.

27 J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *New J. Chem.*, 1998, 1525.

28 X.-P. Yang, R. A. Jones, W.-K. Wong, V. Lynch, M. M. Oye and A. L. Holmes, *Chem. Commun.*, 2006, 1836.

29 (*a*) G. Novitchi, J.-P. Costes and B. Donnadieu, *Eur. J. Inorg. Chem.*, 2004, 1808; (*b*) J.-P. Costes, G. Novitchi, S. Shova, F. Dahan, B. Donnadieu and J.-P. Tuchagues, *Inorg. Chem.*, 2004, **43**, 7792.

30 R. Gheorghe, M. Andruh, J.-P. Costes and B. Donnadieu, *Chem. Commun.*, 2003, 2778.

31 (*a*) H.-Z. Kou, B. C. Zhou and R.-J. Wang, *Inorg. Chem.*, 2003, **42**, 7658; (*b*) H.-Z. Kou, B. C. Zhou, S. Gao and R. J. Wang, *Angew. Chem., Int. Ed.*, 2003, **42**, 3288; (*c*) T. Shiga, H. Okawa, S. Kitagawa and M. Ohba, *J. Am. Chem. Soc.*, 2006, **128**, 16426.

32 A. M. Madalan, H. W. Roesky, M. Andruh, M. Noltemeyer and N. Stanica, *Chem. Commun.*, 2002, 1538.