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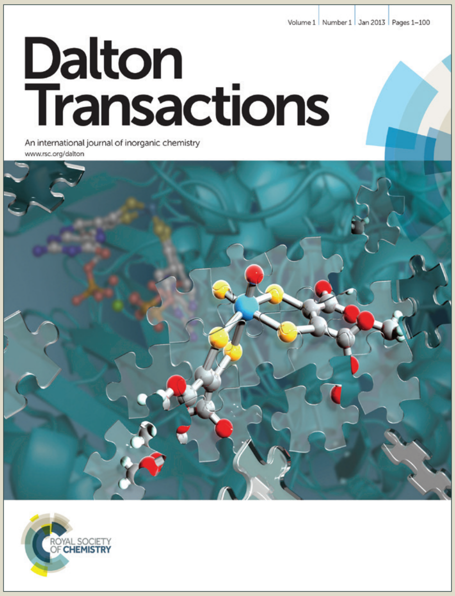

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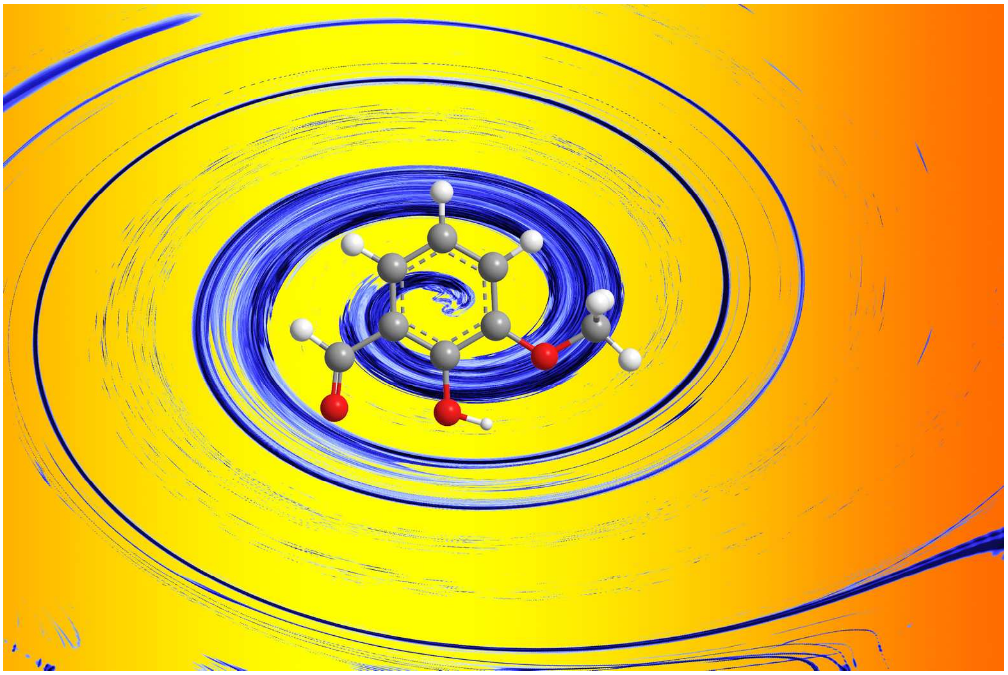

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Perspective

The exceptionally rich coordination chemistry generated by Schiff-base ligands derived from *o*-vanillin

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Ortho-vanillin became very popular in coordination chemistry because of its Schiff bases, which generate a rich variety of complexes, ranging from oligonuclear species to coordination polymers. Some of these organic molecules are particularly useful in metallosupramolecular chemistry for assembling homo- and heterometallic helicates. The Schiff bases obtained using aminoalcohols open the door to the synthesis of homo- and heterometallic clusters with various nuclearities and surprising topologies of the metal centers. Several relevant structural types are reviewed. The hetrobinuclear 3d-3d' and 3d-4f complexes are valuable building-blocks for the synthesis of heterotrimetallic systems. Beyond the richness of this chemistry, the complexes obtained from *o*-vanillin-based Schiff ligands show interesting properties: magnetism, luminescence, chirality, catalysis, cytotoxicity, ferroelectricity. The paper reviews recent data that illustrate a very fertile and dynamic research field in coordination chemistry and materials science.

Introduction

The chemistry of Schiff bases is very generous in providing ligands.[1] The number of amino and keto precursors available for condensation reactions leading to azomethine compounds is practically unlimited. The judicious selection of the two precursors allows a perfect control over: (1) the denticity of the resulting ligands; (2) the nature of the donor atoms; (3) the number of the chelating moieties. Moreover, one or both precursors can be decorated with bulky groups that can further influence the stereochemistry of the metal ions. The increasing interest in homo- and heterometallic oligonuclear complexes in various fields (*e. g*. molecular magnetism, biomimetic coordination chemistry, catalysis) has stimulated the design of ligands able to accommodate a pre-established number of metal ions (compartmental ligands). The first bi-compartmental ligands and their homometallic complexes have been obtained by Robson, using 2,6-diformyl-*p*-cresol and various diamines.[2] When heterometallic complexes are desired, the compartments must be dissimilar (with different sets of donor atoms) and selective, in order to avoid the scrambling of the metal ions. A typical example, representing a family of side-off bi-compartmental ligands, is illustrated in Scheme 1 (the simplest case, H_2valen, is obtained using ethylenediamine). The keto precursor is a derivative of salicylic aldehyde, namely 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin). The methoxy group plays an essential role on the coordination abilities of these molecules. These ligands were employed for the first time by Costes in order to obtain strictly binuclear [$Cu^{II}Ln^{III}$] complexes as models for the investigation of the factors influencing the nature and strength of the magnetic interaction between Cu^{II} and Gd^{III}.[3] The mononuclear copper(II) complex, which reacts in the second step with the lanthanide salt, was reported by Pfeiffer *et al.* in 1933.[4] The inner compartment (N_2O_2) hosts the copper(II) ion, while the open compartment (O_2O_2’) is perfectly appropriate to accommodate the large and strongly oxophilic lanthanide ions. Further on, various bi-compartmental ligands were employed to obtain other binuclear 3d-4f complexes ([$Ni^{II}Gd^{III}$],[5] [$Co^{II}Gd^{III}$],[6] [($V^{IV}O$)Gd^{III}],[7] [$Fe^{II}Gd^{III}$]),[8] as excellent models for magneto-structural correlations. The family of ligands depicted in Scheme 1 is for sure the most appropriate and, consequently, extremely popular to obtain large series of binuclear 3d-4f complexes. The binuclear entities are robust enough to be further employed as building blocks for constructing either high nuclearity clusters or coordination polymers. Moreover, the family of ligands derived from *o*-vanillin has been recently enlarged with new members, able to generate multimetallic complexes with a rich structural variety and intriguing chemical and physical properties. Some representative examples will be discussed herein.

Back to *o*-vanillin as a ligand

The success of the Schiff-base ligands derived from *o*-vanillin drew the attention towards this molecule as an interesting ligand by itself. Indeed, the first homo- and heterometallic complexes containing *o*-vanillin as a main ligand were reported after those containing its Schiff bases. Of course, *o*-vanillin can generate mononuclear bis-chelate species, coordinating through the phenoxido and formyl oxygen atoms to the metal ion, but these compounds are beyond the scope of this review. We will focus here only on several examples where *o*-vanillin (more precisely, its anion, *o*-van$^-$), acts as a bridging ligand.

An interesting family of trinuclear complexes with a triangular topology is formed when a Ln^{III} salt is reacted with *o*-vanillin in the presence of a base: $[Gd_3(\mu_3\text{-}OH)_2(o\text{-}van)_3(NO_3)_2(OH_2)_4](NO_3)_2$,[9] $[Dy_3(\mu_3\text{-}OH)_2(o\text{-}van)_3Cl_2(H_2O)_4][Dy_3(\mu_3\text{-}OH)_2(o\text{-}van)_3Cl(H_2O)_5]Cl_5$,[10] and $[Dy_3(\mu_3\text{-}OH)_2(o\text{-}van)_3Cl(H_2O)_5]Cl_3$.[10] In all these compounds the cationic species consist of triangles of Ln^{III} ions (Figure 1): three *o*-van$^-$ ions form the sides of the triangle, bridging two Ln^{III} ions through the phenoxido group; the aldehyde and the methoxy groups are also coordinated to two metal ions. Two HO$^-$ groups bridge simultaneously three metal ions. The last two Dy^{III} derivatives have remarkable magnetic properties: they show slow relaxation of the magnetization (Single Molecule Magnet, SMM, behavior) in spite of the almost non-magnetic ground state. This behavior arises from the non-collinearity of the single ion easy axes, which form an almost perfect equilateral triangle lying in the Dy_3 plane (toroidal moment).[11] When $LnCl_3$ is reacted simultaneously with *o*-vanillin and the corresponding alcohol, 2-hydroxymethyl-6-methoxyphenol (HL), two Dy_3 triangles are connected by two alkoxo groups from two deprotonated 2-hydroxymethyl-6-methoxyphenol molecules (L$^-$), resulting in hexanuclear clusters, $[Dy_6(\mu_3\text{-}OH)_4(o\text{-}van)_4L_2(H_2O)_9Cl]Cl_5$.[12] The coupling of the two Dy_3 triangles enhances significantly the SMM behavior, with respect to the isolated Dy_3 compounds. A 3d homometallic cluster, $[Co_4(\mu_3\text{-}OMe)_4(o\text{-}van)_4]$, with a heterocubane structure, was obtained by microwave assisted and by solvothermal methods.[13] The cobalt(II) ions are connected by four alkoxido (MeO$^-$) and four phenoxido groups. The interactions between the cobalt(II) ions were found to be ferromagnetic.

Heterometallic complexes can be assembled as well. Two types of Co^{II}-Ln^{III} clusters were obtained by Costes et al. by reacting the mononuclear cobalt complex, $[Co(o\text{-}van)_2(H_2O)_2]$ with Ln^{III} nitrates: $[CoLn(o\text{-}van)_2(H_2O_2(NO_3)_3]$ (Ln = Pr, Gd),[14] and $[(NO_3)_2Ln(o\text{-}van)_2(\mu_3\text{-}HO)Co_2(\mu_3\text{-}OH)(o\text{-}van)_2Ln(NO_3)_2]$ (Ln = Gd, Tb, Y).[15] The second family crystallizes by slow diffusion of acetone into the methanolic solution of the two components. The structure of complexes $[CoLn(o\text{-}van)_2(H_2O_2(NO_3)_3]$ is very similar to that of the binuclear complexes constructed with the Schiff base ligands shown in Scheme 1. Complexes $[(NO_3)_2Ln(o\text{-}van)_2(\mu_3\text{-}HO)Co_2(\mu_3\text{-}OH)(o\text{-}van)_2Ln(NO_3)_2]$ are tetranuclear, with a defect-dicubane central core (Figure

2). The vertices of the common face are occupied by the two cobalt ions and by the two hydroxido groups that make a triple bridge between two Co^{II} and one Ln^{III} ions. The *o*-van^- ligands are coordinated through the formyl, phenoxido and methoxy groups to two metal ions (Co^{II} and Ln^{III}), the phenoxido group acting as a bridge between the metal ions. For the $[Co_2Gd_2]$ derivative both Co^{II}-Co^{II} and Co^{II}-Gd^{III} exchange interactions are weak ferromagnetic (J_{CoCo} = 0.40 cm^{-1}; J_{CoGd} = 0.42 cm^{-1}). The magnetic anisotropy brought by the Co^{II} ions induces a SMM behavior for this compound, confirmed by magnetization *versus* magnetic field hysteresis loops.

Binuclear 3d-4f complexes with compartmental ligands. Recent achievements

Twenty years after the synthesis of the first binuclear 3d-4f complexes with compartmental Schiff-base ligands (Scheme 1), this chemistry is still of interest. First of all, the systematic investigation of the magnetic properties of the whole series gave information on the nature of the exchange interaction between a 3d metal ion (e. g. Cu^{II}, Ni^{II}, Co^{II}) and the other Ln^{III} ions, not only Gd^{III}. These cases are more complicated, because of the strong spin-orbit coupling of the Ln^{III} ions (except Gd^{III}) that makes more difficult the observation of the nature of couplings: the depopulation of the M_J levels for individual Ln^{III} ions, that is, the decrease of their magnetic moment with the temperature, can mask the 3d-4f interaction. A straightforward experimental approach allowing identifying the nature of the M^{II}-Ln^{III} magnetic coupling consists of comparisons of the magnetic behaviors of pairs of $[M^{II}Ln^{III}]$ and $[Zn^{II}Ln^{III}]$ complexes. Recently, we carried out such a study for $[Ni^{II}Ln^{III}]$ binuclear complexes which belong to four slightly different structural types (the compartmenta ligand, H_2valpn, results from the condensation reaction between *o*-vanillin and 1,3-propanediamine).[16a]

Type I.1 - $[Ni(CH_3CN)_2(valpn)Ln(NO_3)_3]$: La, Pr
Type I.2 - $[Ni(CH_3CN)_2(valpn)Ln(NO_3)_3]\cdot CH_3CN\cdot 2H_2O$: Sm
Type I.3 - $[Ni(CH_3CN)_2(valpn)Ln(NO_3)_3]\cdot CH_3CN$: Eu, Gd, Er
Type II -
$[Ni(CH_3CN)_2(valpn)Ce(NO_3)_3(H_2O)][Ni(CH_3CN)(H_2O)(valpn)Ce(NO_3)_2(H_2O)]\cdot NO_3\cdot 2CH_3CN\cdot$: Ce
Type III - $[Ni(CH_3CN)_2(valpn)Nd(NO_3)_3][Ni(CH_3CN)(H_2O)(valpn)Nd(NO_3)_3]\cdot CH_3CN\cdot \frac{1}{2}H_2O$: Nd
Type IV - $[Ni(CH_3CN)(H_2O)(valpn)Ln(NO_3)(H_2O)_3]\cdot (NO_3)_2\cdot CH_3CN\cdot H_2O$: Tb, Dy

The differences between the structures of the members of this series arise from the nature of the axial ligands (solvent molecules) coordinated to the Ni^{II} ions (one aqua and one acetonitrile or two acetonitrile molecules) or from the partial replacement of the nitrato ligands by aqua ligands to the Ln^{III} ions. The structure of a representative complex is illustrated in Figure 3. The series of $[(valpn)Zn^{II}Ln^{III}(H_2O)(NO_3)_3]$ complexes was synthesized and characterized as well.[16b] The crystallographic investigation revealed two structural types: the first one, $[Zn(H_2O)(valpn)Ln^{III}(O_2NO)_3]$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy**)** contains 10-coordinated Ln^{III} ions, while within the second one, $[Zn(ONO_2)(valpn)Ln^{III}(H_2O)(O_2NO)_2]\cdot 2H_2O$ (Ln = Tb, Dy, Ho, Er, Tm, Yb), the rare earth ions are 9-coordinated. Interestingly, crystals belonging to these two structural types were obtained simultaneously for the [ZnTb] and [ZnDy] systems (Figure 4).

The magnetic properties for the [NiLn] complexes ($\chi_M T$ vs. T curves) are shown in Figure 5. It is clearly observed that for the [NiGd], [NiDy] and [NiHo] systems the 3d-4f couplings are ferromagnetic. For the other cases, the nature of the exchange interaction between Ni^{II} and lanthanides displaying spin-orbit coupling can be emphasized by a general procedure that consists of representing the temperature dependence of the difference $\Delta\chi_M T = \chi_M T_{(NiLn)} - \chi_M T_{(ZnLn)}$, where the intrinsic magnetic behavior of the lanthanide ions, as found within the dinuclear $[Zn^{II}Ln^{III}]$ complexes, is subtracted from the one measured for the $[Ni^{II}Ln^{III}]$ complexes. In Figure 6 are shown the results obtained by this procedure for the Pr^{III} and Er^{III} derivatives, as examples for antiferromagnetic and ferromagnetic $[Ni^{II}Ln^{III}]$ interactions, respectively. The Ni^{II}-Tb^{III} coupling was found to be ferromagnetic. The [NiDy] complex shows slow relaxation of the magnetization in the presence of an applied dc field.

The [ZnLn] systems are also interesting because of their luminescence properties, the $\{Zn(valpn)(H_2O)\}$ moiety acting as an efficient antenna. We recall here two particular cases. The first one concerns the europium(III) derivative, $[Zn(H_2O)(valpn)Eu^{III}(O_2NO)_3]$. We were intrigued by the absence of the antenna effect at room temperature not only for this compound, but also for other [ZnEu] complexes with Schiff base ligands derived from the *o*-vanillin.[17] For $[Zn(H_2O)(valpn)Eu^{III}(O_2NO)_3]$, at room temperature, the strongest $^5D_0$ europium emission was observed only by direct excitation, using 535 nm excitation wavelength. By decreasing the temperature to 80 K, the strongest emission of europium was obtained by exciting into the maximum of a high-intensity, low-lying ligand to metal charge–transfer band (LMCT) located at

~420 nm. The significant temperature-induced changes of the photophysical properties of europium were assigned to the presence of a high intensity 420 nm centered LMCT state and the $^3\pi\pi^*$ ligand state close to the $^5D_0$ emissive europium level. The role of the LMCT is not surprising, since europium can easily reach the oxidation state II. The second case is represented by two complexes showing two-photon induced emission, $[Zn(H_2O)(Me_2valpn)Sm(O_2NO)_3]$ and $[Zn(H_2O)(Me_2valpn)Tb(O_2NO)_3]$ (H_2Me_2valpn results from the condensation between *o*-vanillin and 3,2-dimethyl-1,3-diaminopropane). Following femtosecond Ti : Sapphire laser at λ_{ex} = 775 nm, both second-harmonic generation at λ_{em} = 775/2 nm and two-photon induced emission in the VIS range were obtained, extending thus the excitation range of these complexes from the VIS to NIR spectral range (Figure 7).[18] Numerous other families of [ZnLn] complexes were synthesized using bi-compartmental ligands derived from *o*-vanillin and various diamines and their luminescence properties were investigated.[19]

The binuclear $[M^{II}Ln^{III}]$ complexes described above are obtained by reacting the mononuclear 3d precursor with lanthanide nitrates. Recently, Matsumoto *et al.* obtained binuclear complexes using $[Ln(CH_3COO)(Hhfac)(hfac)_2(H_2O)_2]$ instead of $Ln(NO_3)_3$: $[M(MeOH)_x(valpn)Ln(CH_3COO)(hfac)_2]$ (M = Co, Ni, Cu, Zn).[20] The crystal structure of one of these complexes is presented in Figure 8. The two $hfac^-$ ligands are coordinated to the Ln^{III} ion, while the acetato ligand acts as a bridge between the 3d and 4f metal ions. The acetate group can be easily replaced by other anionic ligands, for example azido.[21] The $[Ni^{II}Dy^{III}]$ derivative, $[Ni(N_3)(H_2O)(valpn)Dy(hfac)_2(H_2O)]\cdot H_2O$, shows field induced SMM behavior.

Amirkhanov *et al.* have obtained binuclear [ZnLn] and [NiLn] complexes with $valen^{2-}$ and $valpn^{2-}$ ligands, in which the lanthanide ions are coordinated by the open compartment of the organic ligand and by one or two bidentate carbacylamidophosphate (CAPh) ions - Scheme 2,[22] They illustrated for the first time the ability of these complexes to act as catalysts for phosphodiester hydrolysis (Scheme 3).

The [ZnLn] complexes (Ln = Tb, Dy, Ho) are very attractive since they combine at least two interesting physical properties: luminescence and slow relaxation of the magnetization. Other properties, such as chirality, can be added by choosing appropriate ligands. For example, Long *et al*. designed a chiral [ZnDy] complex using the enantiopure ligand resulted from the condensation of *o*-vanillin with 2,2'-diphenyl-ethylenediamine.[23] Apart from luminescence and Single Ion Magnet (SIM) behavior, this compound crystallizes in a non-centrosymmetric space group and shows ferroelectric properties up to 563 K, the highest temperature for a molecular material.

The $[M(solv)_x(valpn)Ce(NO_3)_3]$ complexes (M = Mn, Fe, Co, Ni, Cu) have found an interesting application for obtaining monodisperse transition-metal substituted CeO_2 nanoparticles, $M_{0.1}Ce_{0.9}O_{2-x}$, which are employed as catalysts.[24] The synthetic procedure consists in the pyrolysis of a mixture containing the heterometallic complex and the complex of Ce(III) with the same Schiff-base ligand ($valpn^{2-}$) in oleylamine at 180 ºC. These mixtures ensure the close association of the two metal ions during the nucleation and growth of the monodisperse, phase-pure nanocrystals of $M_{0.1}Ce_{0.9}O_{2-x}$.

Homometallic lanthanide complexes with valen-type ligands

The hexadentate ligands derived from *o*-vanillin and diamines can generate homometallic lanthanide complexes as well. They coordinate to the Ln^{III} ions solely through the oxygen atoms or through both N and O donor atoms. The first case is in line with the strong oxophilic character of the Ln^{III} ions and two possibilities can be predicted: (i) the ligand preserves its bi-compartmental *cisoid* conformation, but only the $O_2O'_2$ compartment is occupied by the metal ion; (ii) the ligand acts bis-chelating trough the phonoxido- and methoxy oxygens, bridging two lanthanide ions (*transoid* conformation). In most of the reported examples, the protons migrate from the phenolic groups to the imino nitrogen atoms. For example, the reaction of H_2valmen with neodimium nitrate affords a mononuclear complex, $[Nd(H_2valmen)(NO_3)_3]$, in which the Nd^{III} ion is coordinated $O_2O'_2$ atoms from the open compartment and by six oxygen atoms arising from the chelating nitrato ligands (H_2valmen results from the reaction between *o*-vanillin and 1,2-diaminopropane) – Scheme 4a.[25] On the other hand, the reaction between H_2valpn and $Ln(NO_3)_3$ (Ln = Sm, Gd, Lu) led to binuclear complexes, the Ln^{III} ions being connected by bis-chelating H_2valpn ligands: $[Ln(H_2valpn)(NO_3)_3]_2$ (Scheme 4b).[26] The ligands with *transoid* conformation can also generate 1-D coordination polymers (Scheme 4c).[26] In all these example, the imino nitrogen atoms are protonated.

The anion of the lanthanide salt and the nature of the diamine employed to synthesize the Schiff-base can influence the structures of the resulting complexes. The reactions of H_2valchx (obtained using 1,2-cyclohexanediamine) with lanthanide salts (chlorides, acetates, nitrates) led to three families of tetranuclear complexes (Scheme 5):

$[Ln_4(valchx)_2(Hvalchx)_2(\mu_3\text{-}OH)_2Cl_2]Cl_2$ (Ln = Nd, Yb, Er. Gd);[27a]
$[Ln_4(valchx)_2(\mu_3\text{-}OH)_2(CH_3COO)_6]$ (Ln = Nd, Yb, Er, Gd);[27a]
$[Ln_4(valchx)_2(Hvalchx)_2(NO_3)_2(\mu_3\text{-}OH)_2](NO_3)_2$ (Ln = Dy, Tb, Ho, Er).[27b]

In these complexes, part or all the organic ligands involve the nitrogen atoms in the coordination. $[Ln_4(valchx)_2(Hvalchx)_2(NO_3)_2(\mu_3\text{-}OH)_2](NO_3)_2$ is a SMM with the energy barrier U_{eff} = 48.14 K. The neodymium and ytterbium derivatives from the chlorido and acetato series show strong NIR luminescence. Other similar Tb^{III}, Dy^{III}, and Ho^{III} tetranuclear complexes, with the same ligand and starting from lanthanide chlorides, were reported very recently by Li *et al.*[27c]

The inner compartment of the valen-type ligands has been enlarged using diethylenetriamine for the condensation reaction.[28] The resulted $valdien^{2-}$ ligand can now accommodate the large Ln^{III} ions. Murugesu *et al.* characterized a large family of binuclear complexes: $[Ln_2(valdien)_2(X_2)]$ (X = NO_3, CH_3COO, $ClCH_2COO$, $CHCl_2COO$, acac, hfac), the structure of one of them, $[Dy_2(valdien)_2(NO_3)_2]$,[28b] being shown in Figure 9. In all these complexes, the Ln^{III} is hosted into the N_3O_2 compartment and are bridged by the two phenoxido oxygen atoms. The coordination sphere of the Ln^{III} ions is filled by two other oxygen atoms arising from the oxoanions, X^-. For the gadolinium derivative, $[Gd_2(valdien)_2(NO_3)_2]$, the interaction between the metal ions was found antiferromagnetic (J = -0.178(1) cm^{-1}, $\boldsymbol{H} = -J\boldsymbol{S}_{\text{Gd1}}\boldsymbol{S}_{\text{Gd2}}$). The dysprosium analogue is a SMM with a high energy barrier (U_{eff} = 76 K).

For the valen-like ligands derived from 5-bromo-2-hydroxy-3-methoxybenzaldehyde and 1,2-phenylenesiamine, the aggregation of triple- and tetra-decker complexes was observed.[29] The intramolecular π–π stacking interactions established between the phenylene rings enhance the stability of the multi-decker architecture. In these complexes, the Ln^{III} ions are coordinated by both nitrogen and oxygen atoms, and are sandwiched between two ligands.

Heterometallic 3d-3d' complexes

At first glance, the large open compartment, $O_2O'_2$, of the valen-type ligands is not appropriate for hosting the small 3d cations. Moreover, the relative position of the four oxygen atoms does not favor "classical" coordination geometries adopted by 3d metal ions (octahedral, tetrahedral, square planar). However, a 3d metal ion with no stereochemical preference, for example Mn^{II}, can be easily hosted into the $O_2O'_2$ compartment. Indeed, the reaction of the mononuclear copper(II) complex, [Cu(valpn)] with manganese(II) nitrate affords the discrete, binuclear complex $[Cu(valpn)Mn((O_2NO)_2]$, the Mn^{II} ion being eight-coordinated.[30a] We have shown that Co^{II} can be also hosted into the $O_2O'_2$ compartment:[30] The two structures are illustrated in Figure 10.

Oligonuclear 3d-4f complexes with bi-compartmental ligands as building blocks for constructing high-nuclearity clusters and coordination polymers.

Within the binuclear $[M^{II}Ln^{III}]$ species, both metal ions have easily accessible coordination sites, that is, weakly bonded ligands which can be replaced by other ligands. Consequently, they can be employed as tectons for obtaining more complex systems. Moreover, the two metal ions differ drastically in their chemical behaviour: the rare-earth cations are hard acids, with a strong oxophilic character and high coordination numbers, whereas Ni^{II} and Cu^{II} are borderline acids with a marked tendency to adopt an octahedral geometry (Ni^{II}) and a more or less distorted square-pyramidal geometry (Cu^{II}). This means that the two metal ions can interact selectively with various spacers: the lanthanide ions will prefer the ligands bearing oxygen atoms, while the 3d metal ions will preferentially interact with nitrogen ligands. However, the coordination of the lanthanide ions by nitrogen ligands or that of the 3d metal ion by oxygen ligands cannot be excluded. Both high-nuclearity clusters and coordination polymers can be assembled. Most of these systems have been reviewed by us in previous papers.[31] Here we illustrate the versatility of the $[M^{II}Ln^{III}]$ tectons with some very recent examples.

The first case concerns the aggregation of dodecanuclear oxalato-bridged clusters through the slow decomposition of the *L*-ascorbic acid into oxalate ions.[32] The binuclear precursors, $[M^{II}Ln^{III}]$ (M = Ni, Cu, Zn), were assembled by reacting [(M(valpn)] complexes with lanthanide acetates. Their reaction with *L*-ascorbic acid in the presence of triethylamine affords dodecanuclear $[M^{II}{}_6Ln^{III}{}_6]$ clusters with a similar topology (Figure 11). The 3d and 4f metal ions are hosted into the two compartments of the organic ligand ($valpn^{2-}$) like in all the binuclear 3d-4f complexes with side-off compartmental ligands derived from *o*-vanillin. The acetato groups bridge the 3d and 4f metal ions within the same binuclear moiety, while the oxalato ligands connect the 4f ions from different binuclear units (bis-chelating bridging mode), resulting in a neutral, cyclic dodecanuclear complex. Within the $[Zn_6Ln_6]$ and $[Cu_6Ln_6]$ clusters, the 3d metal ions are five-coordinate with a square-pyramidal geometry (two nitrogen and two oxygen atoms from the inner compartment of the organic ligand, forming the basal plane, and one acetato oxygen atom into the apical position). In the case of the [Ni_6Ln_6] complex, the nickel(II) ions show an octahedral stereochemistry.

Two interesting clusters were obtained connecting binuclear [Cu^{II}(valen)Ln^{III}] entities by polyoxoanions, namely A- and B-type Anderson ions: [{Cu(valen)Ln(H_2O)$_3$}$_2${IMo_6O_{24}}]Cl·and [{Cu(valen)Tb(H_2O)$_2$}$_2${$AlMo_6O_{18}(OH)_6$}$_2$] (Figure 12).[33] Within the first compound, the two [CuTb] units are bridged by one POM ligand, while within the second compound two binuclear units are bridged by two POM ligands. Both compounds show SMM behavior with U_{eff} = 17.1 and 20.8 K, respectively, while the binuclear precursor does not show the slow relaxation of the magnetization. The substitution of the chlorido ligands from the binuclear precursor, [Cu(valen)Tb(H_2O)$_3$$Cl_2$]Cl, by the POM anions strongly influences the crystal field symmetry around the Tb^{III} ions and thus enhances the magnetic anisotropy.

The self-assembly process involving [M(valpn)Ln(solv)$_x$]$^{3+}$ and N_3^- ions afforded tetarnuclear clusters, [M_2(valpn)$_2$$Ln_2$($N_3$)$_6$] (M = Cu, Zn; Ln = Gd, Tb), in which the Ln^{III} ions from the {M(valpn)Ln} units are bridged by two end-on azido groups (Figure 13).[34] The [Cu_2Tb_2] derivative is a SMM with hysteresis loops observed below 2.4 K.

The uptake of the atmospheric CO_2 during the crystallization processes involving [$M^{II}Ln^{III}$] species resulted in quite interesting clusters with carbonato bridges. For example, the slow evaporation of acetone/methanol solutions containing [Zn(valpn)Ln(NO_3)$_3$] (Ln = Gd, Tb, Dy), in the presence of triethylamine, afforded crystalline materials consisting of μ_4-carbonato bridged tetranuclerar complexes: [{Zn(valpn)Ln(O_2NO)}$_2$(CO_3)$_2$] – Scheme 6.[35a] A simiar tetranuclear bis-carbonato-bridged complex was obtained starting from the [Ni(valpn)Gd] derivative.[35b] By carrying out the crystallization in the presence of azide ions, we obtained linear octanuclear [Ni_4Ln_4] complexes (Ln = Sm, Gd) with both azido and carbonato bridges.[36] The crystal structure of the gadolinium derivative is shown in Figure 14. The weak competitive exchange interactions, J_{GdGd}, J_{GdNi}, J_{NiNi}, make the ground state of this magnetic system degenerate at cryogenic temperature and zero field. This, along with the big spin of Gd^{III} lead to a significant magnetocaloric effect spread in the temperature range 1 - 20 K, with -ΔS_m[0-7 T, 3.5 K] = 19 J Kg^{-1} K^{-1}.

The oligonuclear 3d-4f complexes are particularly attractive for synthesizing, in a rational way, heterotrimetallic complexes. Indeed, the synthetic approach is straightforward and relies on the use of metalloligands, which carry the third metal ion. Anionic cyanido-complexes, either homo- or heteroleptic, are very popular in this respect. Moreover, while looking for interesting magnetic properties, the cyanido bridge is an excellent mediator for the exchange interactions. The complexity of these properties increases when the three different metal ions are paramagnetic. The simplest case is the one of a trinuclear complex containing three different metal ions. Such a complex was obtained by us: $[\{(bipy)W(CN)_6\}Cu(valpn)Gd((H_2O)(O_2NO)_2]$, where the heteroleptic metalloligand, $[W^V(bipy)(CN)_6]^-$, is coordinated through one of its cyanido ligands into the apical position of the copper(II) ion (Figure 15).[37] The investigation of the magnetic properties reveals a ferromagnetic Cu^{II}-Gd^{III} coupling, and an antiferromagnetic Cu^{II}-W^V interaction across the cyanido bridge (Figure 16 shows the temperature dependence of the $\chi_M T$ product for this compound): $J_{CuGd} = +8,67\ cm^{-1}$, $J_{CuW} = -1.52\ cm^{-1}$, $\boldsymbol{H} = -J_{CuGd}\boldsymbol{S}_{Cu}\boldsymbol{S}_{Gd} - J_{CuW}\boldsymbol{S}_{Cu}\boldsymbol{S}_{W}$. Other trinuclear 3d-5d-4f complexes, $[Ni^{II}Ln^{III}W^V]$, with a similar topology, were obtained by Sutter *et al.*, employing Me_2valpn^{2-} (*o*-vanillin plus 2,2'dimethyl-1,3-propanediamine) as a compartmental ligand, and $[W(CN)_8]^{3-}$ as a metalloligand.[38] The octacyanidotungstate is coordinated through one CN group into one apical position of the Ni^{II} ion. Both Ni^{II}-W^V and Ln^{III}-Ni^{II} (Ln = Gd, Tb, Dy, Er) were found to be ferromagnetic (for the Gd^{III} derivative: $J_{NiW} = 27.1$, $J_{NiGd} = 2.17\ cm^{-1}$; the Tb^{III} derivative is a SMM)). Recently, Kou *et al.* have obtained cyclic hexanuclear complexes by assembling $[Ni(H_2O)_2(valpn)Dy(H_2O)_n]^{3+}$ and $[Fe(CN)_6]^{3-}$ ions:[39] $[Ni(valpn)(H_2O)Dy(H_2O)_3Fe(CN)_6]_2\cdot 8H_2O$ (Figure 17a). Each $[Fe(CN)_6]^{3-}$ is coordinated simultaneously to one Ni^{II} and one Dy^{III} ion, through two *cis*-cyanido groups. This compound is a SMM, with $U_{eff} = 17.9$ K, under an applied static field (2000 Oe).

During the self-assembly processes, a second $[M^{II}L]$ unit can coordinate to the lanthanide ion, resulting in trinuclear $[M^{II}Ln^{III}M^{II}]$ species (Scheme 7).[40] This process is favored by poorly coordinating anions or by the pre-established molar ratio $[M^{II}L]$: Ln^{III} = 2 : 1.[39] Using another valen-like ligand, Me_2valpn^{2-}, a molar ratio $\{Ni(Me_2valpn)\}$: Dy^{III} = 2 : 1, and $[Fe(CN)_6]^{3-}$ as a metalloligand, the octanuclear cluster $[\{Ni(Me_2valpn)\}_2Dy(H_2O)Fe(CN)_6]_2\cdot 14H_2O\cdot 4DMF$ was assembled (Figure 17b), which is a SMM with $U_{eff} = 25$ K in zero static field.

Hetrotrimetallic coordination polymers can be assembled as well. There are no rules to predict whether oligonuclear complexes or coordination polymers will be assembled. Both systems can be obtained irrespective the nature of the metalloligand (homo- or heteroleptic). Our first heterotrimetallic polymers were constructed by connecting binuclear nodes, {Cu(valpn)Ln}, through homoleptic $[M(CN)_6]^{3-}$ metalloligands: $^{\infty}{}_1[\{CuL\}Gd(H_2O)_3\{M(CN)_6\}]\cdot$(M = Cr, Fe, Co).[41] By reacting [Cu(valpn)] with $Ln(NO_3)_3$ and $(NHBu_3)_3[M(CN)_8]$, we obtained again 1-D heterotrimetallic coordination polymers, the resulting nodes being in this case trinuclear, {Cu(valpn)Ln(valpn)Cu}, as shown in Figure 18a (M = Mo, W; Ln = Gd, Tb, Dy).[42] The dysprosium derivative is a Single Chain Magnet (SCM). We observed that the nature of the diamine used to obtain the Schiff-base ligand induces important structural changes with the resulting heterotrimetallic complexes. For example, starting from [Cu(valen)] instead of [Cu(valpn)], we obtained simultaneously two compounds: a discrete heterometallic trinuclear complex, $[\{W(CN)_8\}Cu(valen)Tb(OH_2)_5]$, and a 1-D coordination polymer with binuclear {Cu(valen)Tb} nodes, $[\{W(CN)_8\}Cu(valen)Tb(OH_2)_4]\cdot$ (Figure 18b,c).[43] Both compounds show slow relaxation of the magnetization.

The number of heterotrimeatllic complexes of interest in molecular magnetism is increasing but does not exceed 100 examples. Among these, the 2-D networks are very rare. An isostructural family of heterotrimetallic 2-D polymers was assembled from $\{Ni^{II}(valpn)Ln^{III}\}^{3+}$ (Ln = Gd, Tb, Dy) and $\{Fe^{III}(bipy)(CN)_4\}^-$ tectons (Figure 19).[44]

Helicates

An interesting family of ligands obtained through Schiff condensation is represented by the helicands, which are linear strands with repeating complexation sites separated by suitable spacers.[45] The diamine employed must by linear/rigid, in order to prevent the “closure” of the bicompartmental ligand. The metallohelicates are assembled by twisting the multidentate organic ligands (helicands) through the interaction with the metal ions. The helicands derived from *o*-vanillin are tetratopic and, in principle, can generate tetranuclear helicates. Moreover, since the coordination sites are not equivalent, these ligands are appropriate for obtaining heterometallic helicates. For example, Costes *et al.* assembled double-stranded helicates containing two $Cu^{II}Ln^{III}$ pairs with helicands obtaind from the condensation of 4,4′-diaminodiphenylmethane with *o*-vanillin or with 3-ethoxysalicylaldehyde.[46] The crystal structure of the $[Cu_2Gd_2]$ helicate derived from 3-ethoxysalicylaldehyde has been solved (Figure 20).[46b] The isostructural helicate, $[Cu_2Tb_2]$, shows slow relaxation of the magnetization and magnetic hysteresis loops.

Starting for *o*-vanillin and 4,4’-diaminodiphenylether we obtained a family of similar binuclear double-stranded helicates, using Co^{II}, Cu^{II}, and Zn^{II} as assembling cations.[47] The metal ions have a distorted tetrahedral geometry, being coordinated by two phenoxido oxygen atoms and by two imino nitrogens. The crystal structure of the cobalt(II) helicate is displayed in Figure 21. The case of the cobalt(II) helicate is particularly interesting from the magnetic point of view. The large intramolecular distance between the metal ions is large (11.59 Å), precluding any magnetic coupling. On the other hand, dynamic susceptibility measurements indicate the occurrence of slow relaxation of the magnetization in the presence of an applied dc field (Figure 22a). The Arrhenius plot (Figure 22b) shows that the relaxation process does not follow the simple linear behavior. The high temperature data were fitted to the Arrhenius low: (τ_0 = 2.5(3) × 10^{-7} s, U_{eff} = 26(1) K), while the low temperature ones were fitted to a $\tau = aT^n$ law, with n= -2.15±0.05. In order to get more information, the magnetic properties of the doped sample, $Zn_{0.98}Co_{0.02}$, were investigated: no χ’’ signal is observed, either in zero or applied field, indicating that the slow relaxation process observed in the pure sample disappears. All these data suggest that the slow magnetic relaxation observed in the pure compound is not intrinsic to the two tetrahedral Co^{II} centers, but is due to collective phenomena. This behavior was attributed to phonon bottleneck effects,[48] with relaxation times following a $\tau = aT^n$ dependence, where $n = -2$.

The case of the zinc helicate is also interesting, but from another perspective: due to the rigidization of the two organic ligands upon coordination, it exhibits fluorescence emission in solution (Figure 23). The highest quantum yield (Φ = 4.47%) was observed in chloroform.

Binuclear Dy^{III} quadruply stranded helicates were assembled from helicands resulted from the 2 : 1 condensation of *o*-vanillin with benzene-1,4-diamine or 4,4’-methylenedianiline (Figure 24).[49] When the Schiff base is obtained from biphenyl-4,4’-diamine, a binuclear mesocate is obtained. Within the three compounds each Dy^{III} moiety acts as a Single Ion Magnet.

Although *m*-phenylene diamine is a rigid molecule, the resulting Shiff-base ligand does not form a helicate, as shown by Colacio *et al.*, who obtained tetranuclear [Ln^{III}Ni^{II}Ni^{II}Ln^{III}] complexes (Ln = Gd, Dy), with two {Ln^{III}Ni^{II}} halves connected by the *m*-phenylene group.[50] As in many other Ni^{II}Ln^{III} complexes, the exchange interaction is ferromagnetic; the Ni^{II}···Ni^{II} coupling, mediated by the *m*-phenylene group, is ferromagnetic as well (spin polarization effect). This work illustrates, once more, that, by replacing a lanthanide with another one, various magnetic properties can be designed (a significant magnetocaloric effect for the [Ni_2Gd_2]

complex and slow relaxation of the magnetization for the [Ni_2Dy_2] one). Actually, this is part of a more general strategy: within the same family of 3d4f complexes, the 3d and 4f metal ions are chosen in order to reach specific physical properties: luminescence ([ZnLn] complexes), SMMs ([MTb], [MDy], [MHo]), magnetocaloric effect (gadolinium derivatives).

A particular case of ligands are those obtained using diamines with long, flexible alkyl chains between the two amino groups. For example, the Schiff base resulted from *o*-vanillin and 1,6-hexanediamine acts neither as a compartmental ligand nor as a helicand.[51a] Its reaction with Eu^{III} and Cd^{II} ions affords a very interesting drum-like cluster, with 25 to 30 Å in diameter (Figure 25). The sides of the nano-drum are formed by six –$(CH_2)_6$- chains, while the top and bottom are formed by the phenoxido and methoxy oxygens, as well as by the imine nitrogens, which bind 8 Eu^{III} and 24 Cd^{II} ions. This compound shows luminescence both in solution and solid state, and has a significant cytotoxicity towards lung cancer and gastric cancer cell lines. The same drum-like structures were assembled when Eu^{III} is replaced by Y^{III} or Nd^{III} ions, but the total number of metal ions is different: $\{Ln_6Cd_{24}\}$.[51b]

Tripodal ligands

An alternative way to obtain bicompartmental ligands starting from *o*-vanillin consists in the employment of appropriate triamines (e. g. tris(2-aminoethyl)amine), resulting in tripodal ligands that can accommodate one or two lanthanide ions, either identical or different.[52]

A new generation of Schiff-base ligands

Most of the Schiff-base ligands derived from *o*-vanillin were obtained using primary diamines (2 : 1 condensation). Actually, many other ligands with various denticities can be synthesized playing with the nature of the amino precursor (diamines with one primary and one tertiary amino group, aminoalcohols, aminoacids, etc). Scheme 8 shows two ligands obtained by the condensation reaction between *o*-vanillin and 2-aminomethyl-pyridine and 2-(2-aminoethyl)-pyridine: Hvalampy and Hvalaepy. A much larger family of Schiff bases was obtained using various aminoalcohols (Scheme 9). While the ligands discussed in the previous sections have a quite predictable coordination behavior, the nature of the resulting complexes using the ligands depicted in Schemes 8 and, especially, 9 cannot be easily anticipated. The alkoxide oxygen atom resulted by the deprotonation of the alcoholic group acts either as a terminal ligand or, most frequently, as a bridge, connecting two or three metal ions, and these coordinating modes cannot be controlled. However, these ligands generate serendipitously very interesting homo- and heterometallic clusters. Let us illustrate first the coordination chemistry of the Hvalampy and Hvalaepy ligands. A tetranuclear cluster with a heterocubane {Cu_4O_4} core has been assembled from four Cu^{II} ions and four valampy$^-$ ligands (Figure 26).[53] Both ligands were employed to synthesize 3d-4f complexes. Irrespective the nature of the ligand (Hvalamy, Hvalaepy) and of the 3d metal ion (Ni^{II}, Cu^{II}, Zn^{II}) only binuclear complexes were assembled.[54] The crystal structures of three representative complexes, [Ni(valaepy)$_2$Ln(O_2NO)$_3$(H_2O)], [Cu(valaepy)$_2$Ln(O_2NO)$_3$], and [Zn(valaepy)$_2$Ln(O_2NO)$_3$], are shown in Figure 27. There are subtle structural differences between the first compound and the two others, which arise from the stereochemical preferences of the metal ions: nickel(II) is six-coordinated, with an octahedral geometry, while the copper(II) and zinc(II) ions are five-coordinated. The coordination sphere of Ni^{II} is formed by two azomethynic and two pyridyl nitrogen atom, and by two phenoxo oxygens. The europium and nickel ions are bridged by the two phenoxido oxygens. The coordination number of europium is 9 (two phenoxido oxygen atoms, six oxygens from three chelating nitrato ligands, and one aqua ligand). The two methoxy groups are no more coordinated to the europium ion. This is somehow surprising, since the methoxy groups from the *o*-vanillin moiety play an active role in holding the rare earth cations within heterometallic complexes. In this case, the stereochemical requirements of nickel(II), that is, its strong preference for the octahedral geometry orient the two valaepy$^-$ molecules such that the two methoxy groups are too far from the europium ion to be coordinated. The Cu^{II} and Zn^{II} derivatives are isostructural. The coordination modes of the two ligand molecules towards copper/zinc are different: one of them (valaepy-**A**) is coordinated to the copper/zinc ion through the phenoxido oxygen atom and the two nitrogen atoms, while the second one (valaepy-**B**) is coordinated through the phenoxido oxygen and the azomethynic nitrogen, the pyridyl arm being uncoordinated. Consequently, the copper/zinc ion is pentacoordinated, with a trigonal bipyramidal geometry. The lanthanide ion is located into the open cavity described by the four oxygen atoms arising from the two ligand molecules. The methoxy group from valaepy-**A** is coordinated to the lanthanide ion while the other one, arising from the valaepy-**B** molecule, can be considered as semicoordinated. Taking into account only normal the lanthanide – oxygen distances, the lanthanide ion is ninecoordinated: two bridging phenoxido oxygens, six oxygen atoms from the bidentate nitrato ligands, and one oxygen from the methoxy group.

Without going into details, we mention here that even more simple Schiff bases resulted from *o*-vanillin and monoamines (e. g. methylamine) generate also interesting coordination compounds. Piligkos, Jones *et al.* reported recently on various homo- and heterometallic complexes, ranging from discrete species to 1-D coordination polymers, which are obtained employing the 2-iminomethyl-6-methoxy-phenol as a ligand.[55]

Let us discuss now several representative examples of complexes obtained from the Schiff bases depicted in Scheme 9, the simplest being those derived from monoethanolamine (H_2valmea) and propanolamine (H_2valpa). These ligands generate homometallic (3d or 4f) and heterometallic complexes, with both alcohol and phenol groups deprotonated, or only with the phenol one deprotonated. The presence of different coordinating groups makes these ligands extremely versatile. For example, the reaction of H_2valpa with copper(II) perchlorate in the presence of triethylamine and with manganese(II) acetate affords binuclear alkoxido-bridged complexes: $[Cu^{II}_2(valpa)_2]$[56] and $[Mn^{III}_2(\mu_{1,3}\text{-}OOCCH_3)_2(valpa)_2]$.[57] The manganese(III) derivative acts as a catalyst towards the oxidation with molecular oxygen of 3,5-di-tert-butylcatechol to the corresponding quinone. The same ligand, deprotonated with triethylamine, in reaction with nickel(II) nitrate, generates a heterocubane: $[Ni_4(valpa)_4(CH_3OH)_4]$.[58] A similar compound, $[Ni_4(valmea)_4(CH_3OH)_4]$, is assembled using valmea^{2-} as a ligand.[58] This chemistry can be enlarged using auxiliary ligands: Mohanta *et al.* characterized two complexes resulted from Ni^{II} ions, H_2valmea, and NCO^- or $NCSe^-$ as co-ligands: $[Ni_2(Hvalmea)_3(\mu_{1,1}\text{-}NCO)]$ (only the phonolic groups are deprotonated) and $[Ni_4(valmea)_2(Hvalmea)_2(SeCN)_2(H_2O)_2]$, again a heterocubane.[59]

A family of hexanuclear $[Co^{II}_2Ln^{III}_4]$ clusters (Ln = Eu, Gd, Tb, Dy) has been assembled from Co^{II}, Ln^{III}, and valmea^{2-}, pivalato (piv$^-$) and mea$^-$ ligands: $[Co_2Ln_4(\mu_3\text{-}OH)_2(piv)_4(valmea)_4(mea)_2]$.[60] The coordination modes for the valmea^{2-} ligand are shown in Scheme 10. The gadolinium derivative (Figure 28) has a significant magnetocaloric effect ($-\Delta S_m = 24.9\ Jkg^{-1}K^{-1}$). Slow relaxation of the magnetization was observed for the $[Co_2Dy_4]$ complex.

The Schiff-base ligand resulted from *o*-vanillin and *o*-amino-phenol, H_2valamph, has also a rich coordination chemistry. With Ni^{II} ions it forms a heterocubane, $[Ni_4(valamph)_4(CH_3OH)_2]$, all metal ions being ferromagnetically coupled.[61] As far as the heterometallic systems are concerned, several families of tetranuclear [M_nLn_2] complexes have been characterized (M = Mn^{III}, Ni^{II}, Co^{II}). The structural differences between them arise from the nature of the 3d metal ion, its oxidation state, as well as from the nature of the anion accompanying the 3d metal ion in the staring salt. Hexanuclear clusters, [$Ni_4Ln_2(\mu_3\text{-}OH)_2(valamph)_4(CH_3COO)_2(NO_3)_2(H_2O)_2$] (Ln = Gd, Tb), were obtained in one-pot reaction between nickel(II) acetate, lanthanide nitrates, and the organic ligand in the presence of triethylamine.[62] The crystal structure of the Dy^{III} derivative is shown in Figure 29a: The metal core is made up of two {Ni_2LnO_4} defective heterocubanes. Starting from dysprosium triflate and nickel (or cobalt) nitrate, Kostakis *et al.* synthesized tetranuclear complexes: [$M_2Dy_2(valamph)_4(EtOH)_6$]($ClO_4$)$_2$ with defective cubane structures (M = Co, Ni).[63] Using $NiCl_2$ they obtained another tetranuclear complex: [$Ni_2Dy_2(valamph)_4Cl_2(CH_3CN)_2$]. The crystal structure of [$Ni_2Dy_2(valamph)_4(EtOH)_6$]($ClO_4$)$_2$ is illustrated in Figure 29b. The topology of the metal centers in [$Ni_2Dy_2(valamph)_4Cl_2(CH_3CN)_2$] is similar. This last compound is a very efficient catalyst, in solution, for the synthesis of *trans*-1,5-diaminocyclopent-2-enones from 2-furaldhyde and primary or secondary amines in non-inert atmosphere (Scheme 11). Similar tetranuclear complexes, [$Co^{II}{}_2Ln^{III}{}_2(valamph)_4(NO_3)_2(THF)_2$], with a defect-dicubane (or butterfly) topology have been obtained by Powell *et al.*[64]

Isostructural tetranuclear complexes with the general formula [$Mn^{III}{}_2Ln^{III}{}_2(O)(valamph)_4(CH_3OH)_4(Cl_2)$] were assembled from the reaction between $MnCl_2$, valamph^{2-}, and lanthanide perchlorates (Ln = Eu, Gd, Tb, Dy).[65] The structure of the [$Mn^{III}{}_2Gd^{III}{}_2$] derivative is presented in Figure 30, and can be described as being formed by two equivalent {$Mn^{III}Gd^{III}(valamph)_2(CH_3OH)_2Cl$} moieties, with the lanthanide ions bridged by one μ-O^{2-} ion and by two phenoxido oxygen atoms. The Mn^{III}-Gd^{III} interaction was found to be antiferromagnetic, while the Mn^{III}-Tb^{III} and Mn^{III}-Dy^{III} ones are ferromagnetic. The dysprosium derivative is a SMM with $U_{\mathrm{eff}} = 15.8$ K.

The fourth ligand in Scheme 9, H_2valabz, is obtained from *o*-vanillin and *o*-aminobenzylalcohol. Its reactions with nickel(II) acetate and lanthanide nitrates lead to tetranuclear complexes: [$Ni^{II}{}_2Ln^{III}{}_2(CH_3COO)_3(Hvalabz)_4(H_2O)_2$]($NO_3$)$_3$ (Ln = Dy, Tb, Ho, Lu); in the case of gadolinium and praseodimium, binuclear complexes are assembled: [$Ni^{II}Ln^{III}(Hvalabz)_2(NO_3)_3$].[66] Figure 31 shows the two structural types, the binuclear and tetranuclear complexes, which are related. The structure of the tetranuclear complexes can be seen as being formed by two {$Ni^{II}Ln^{III}(Hvalabz)_2$} halves, triply bridged by acetato ligands.

Again, the main interest in such compounds arises from their magnetic properties: $[Ni^{II}_2Dy^{III}_2(CH_3COO)_3(Hvalabz)_4(H_2O)_2](NO_3)_3$ is a SMM in zero dc field (U_{eff} = 19 K).

Apart from the ligands depicted in Scheme 9, the library of Schiff bases derived from *o*-vanillin and aminoalcohols or amino-acids is much larger, being continuously enriched with new examples. Some of them are gathered in Table 1. Due to their various denticities and versatility, these ligands are able to generate interesting families of homo- and heterometallic clusters.

From bicompartimental ligands to versatile cyanido building-blocks

In spite of the richness of the chemistry based on these ligands, strictly binuclear complexes with a trivalent cation located within the N_2O_2 compartment, $[M^{III}Ln^{III}]$, are unknown. Following the stepwise synthesis of the heterometal complexes, the mononuclear species formed in the first step is cationic and the interaction with the second metal ions is not favored. Only in the case of Fe^{III}, the two compartments are filled by the iron(III) and the lanthanide(III) ions, but the final compounds are tetranuclear species, with the iron(III) ions connected by an oxido bridge: [{LnFe}-O-{FeLn}].[78] A solution to overcome this difficulty could be the addition of anionic ligands on the metal ion within the mononuclear metalloligand. In order to be employed as building-blocks, these anionic species must be stable in solution towards the dissociation of the ancillary ligands, otherwise, the control over the reaction products is not possible. This condition can be fulfilled by choosing a metal ion that forms six very stable metal-ligand bonds. The best candidates are 4d and 5d metal ions. Among these, ruthenium(III) and osmium(III) ions, both paramagnetic, are particularly important in molecular magnetism. Such metalloligands are versatile: they can coordinate the second metal ions either through the $O_2O'_2$ compartment, or through the cyanido groups.

We succeeded to synthesize $[K(H_2O)_2Ru^{III}(valen)(CN)_2]$.[80] Its reactions with lanthanide nitrates afforded a family of isostructural 1-D coordination polymers: $^1_\infty[\{Ru(valen)(CN)_2KRu(valen)(CN)_2\}\{Ln(O_2NO)_2(CH_3OH)_3\}]\cdot$(Ln = Gd, Tb, Dy), where each $[Ru(valen)(CN)_2]^-$ metalloligand is coordinated to the terbium ion through one cyanido group, the other one being terminal. The structure of these compounds can be described as being formed by trinuclear cyanido-bridged units, {Ru-CN-Ln-NC-Ru}, which are connected by the potassium ions, coordinated by two $O_2O'_2$ compartments, resulting in infinite chains (Figure 32). The interaction between Gd^{III} and Ru^{III} ions, bridged by one cyanide group was fond weak and antiferromagnetic (J = -0.33 cm^{-1}, $\boldsymbol{H} = -J\cdot(\boldsymbol{S}_{Ru1}\cdot\boldsymbol{S}_{Gd} + \boldsymbol{S}_{Gd}\cdot\boldsymbol{S}_{Ru2})$).

Conclusions

The main difference between *o*-vanillin and salicylic aldehyde, as well as between their Schiff-bases originates from the presence of the methoxy group that confers the "personality" of these molecules as ligands: the methoxy groups offer additional coordinating sites and strongly influence the nature of the complexes which are assembled. These groups are also essential for designing heterotopic helicands and binucleating tripodal ligands and the corresponding heterometallic complexes. For the mononuclear coordination compounds with valen-type ligands, the $O_2O'_2$ cavity has a marked crown ether-like ability to encapsulate alkali-metal ions. Moreover, the $O_2O'_2$ cavity acts as an excellent hydrogen-bond acceptor, and plays a crucial role in the crystal packing of these molecules with various hydrogen-bond donors.[30a,80]

The great potential of the Schiff bases of *o*-vanillin in coordination chemistry can be understood by simply counting the properties exhibited by the complexes they generate: (1) magnetism (SMMs and SCMs; platforms for magneto-structural correlations); (2) luminescence (visible, NIR, two-photon excitation, second-harmonic generation); (3) chirality; (4) catalysis; (5) cytotoxicity; (6) ferroelectricity. Moreover, some of these compounds combine two useful physical properties, opening new routes towards multifunctional materials. The formation of interesting and unexpected molecules enriches our knowledge on the aggregation of homo- and heterometallic clusters. The binuclear 3d-3d' and 3d-4f complexes are excellent building-blocks for constructing high nuclearity clusters, coordination polymers, as well as heterotrimetallic systems. In spite of the large number of complexes synthesized to date, this chemistry is still far from being exhausted. The organic amines for the Schiff condensation, carrying one or more other coordinating groups, the various combinations of different metal ions, and the employment of auxiliary ligands make this field extremely fertile. The further development of this research area, based on quite simple starting materials and stimulated by the search for exciting properties, is a matter of imagination.

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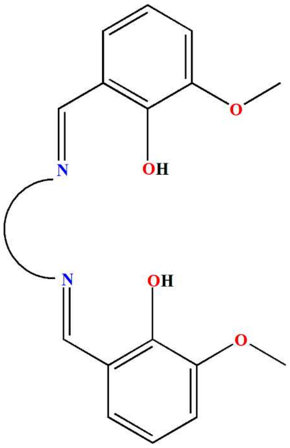
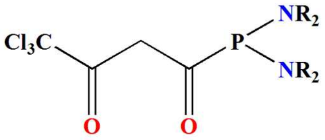


H_2valXn ligands

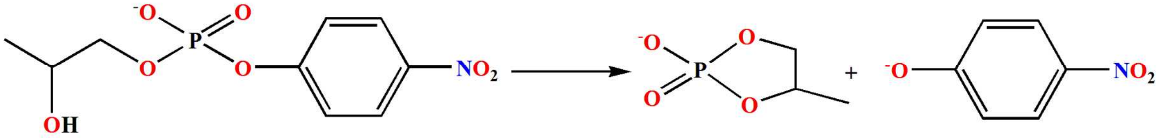
Scheme 1



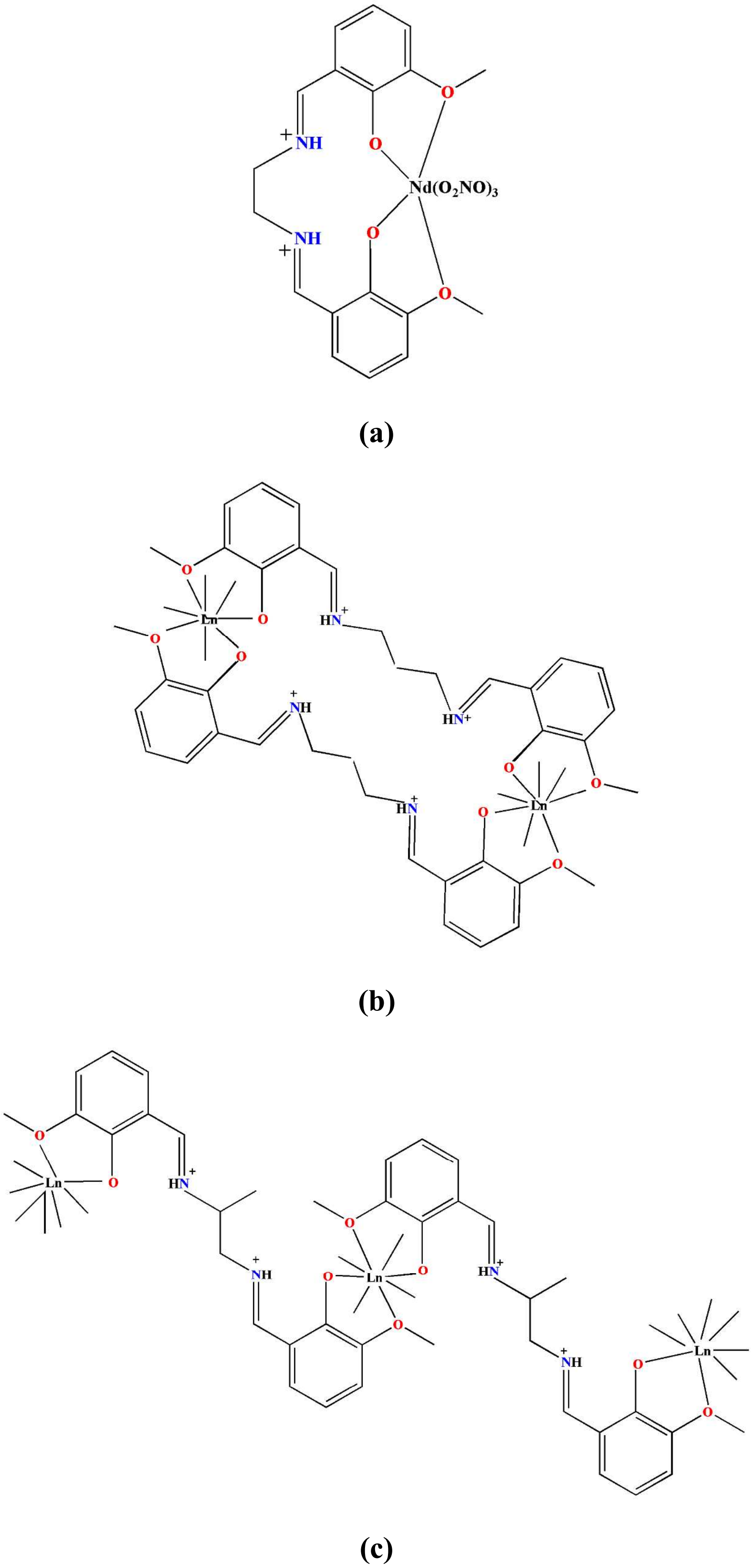
(R = CH_3; C_2H_5)

CAPh ligands

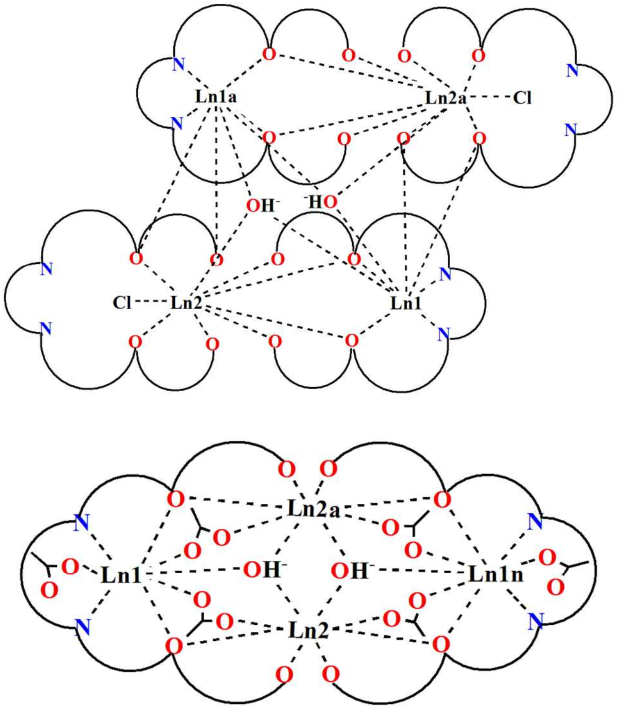
Scheme 2



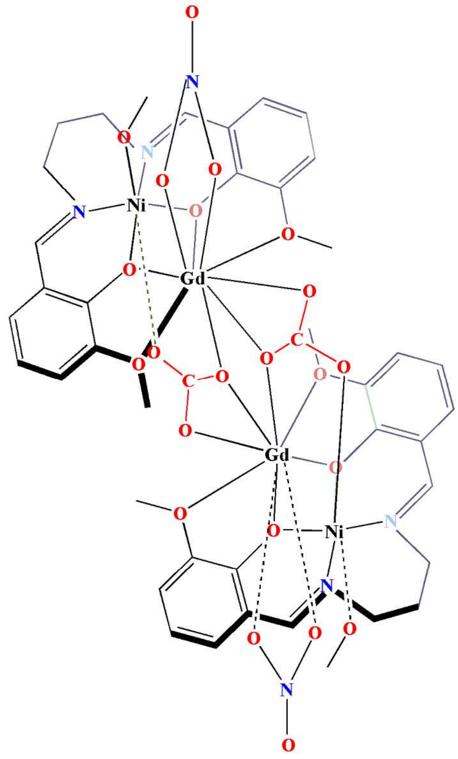
Scheme 3



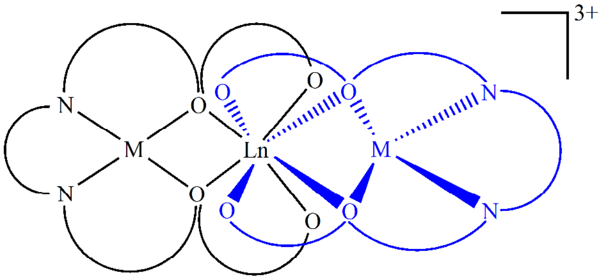
Scheme 4



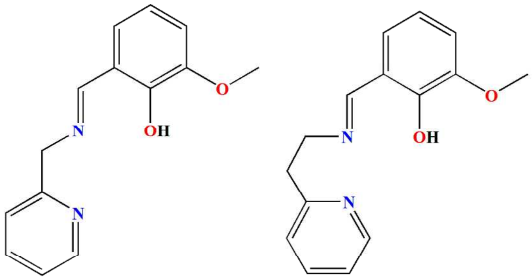
Scheme 5



Scheme 6

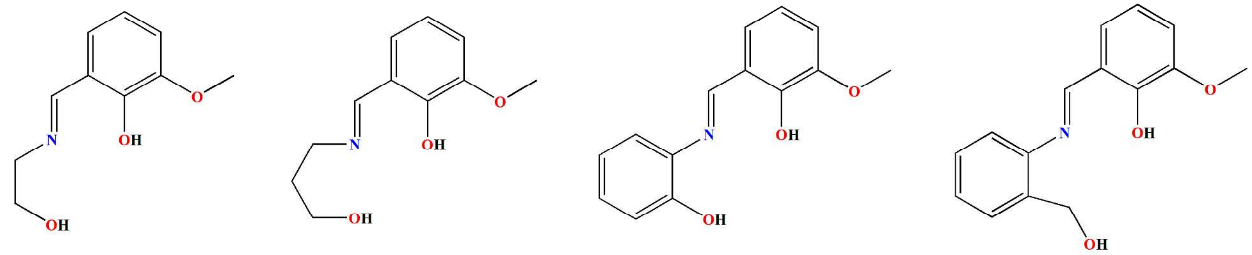


Scheme 7



Hvalampy Hvalaepy

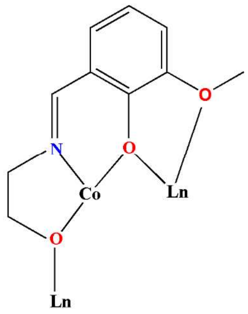
Scheme 8

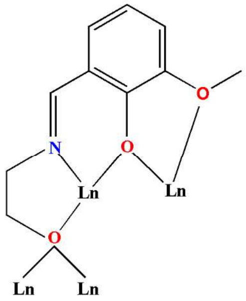


H_2valmea H_2valpa H_2valamph H_2valabz

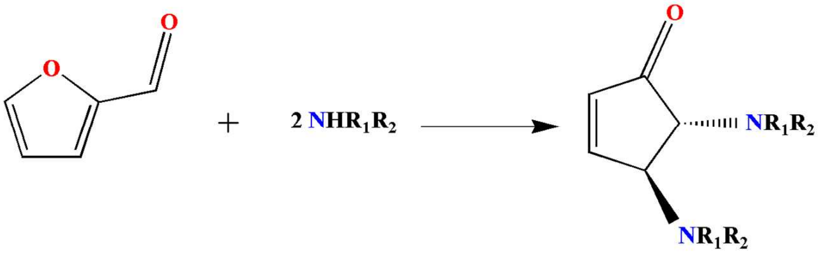
Scheme 9

SCHEMES



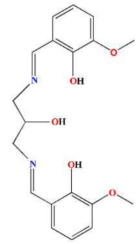
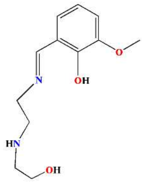
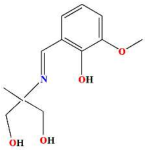
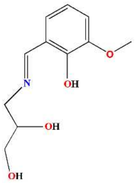
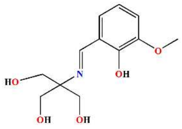
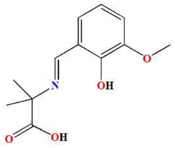


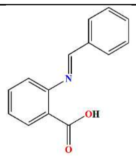
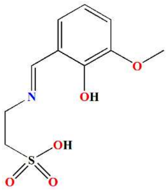
Scheme 10



Scheme 11

Table 1. Schiff-base ligands obtained using aminoalcohols and aminoacids, and their complexes

Ligand	Complexes	Ref.
	$[Cu^{II}_5Ln^{III}_2]$	67
	$[Fe^{III}_4]$, $[Fe^{III}_4Ln^{III}_2]$ $[Co^{III}_2Dy^{III}]$	68 69
	$[Mn^{III}_3Ln^{III}Na^{I}]$	70
	$[Ln^{III}_4]$	71
	$[Co^{III}Co^{II}]$ $[Cu^{II}_5Gd^{III}_3]$ $[Mn^{III}_4Nd^{III}_2]$	72 73 74
	$[Cu^{II}_4]$	75
	$[Dy^{III}_4]$, $[Dy^{III}_8]$	76

	$[Na^{I}_2Ln^{III}_6]$	77
	$[Co^{II}_7]$, $[Na^{I}Co^{II}_3]$	78

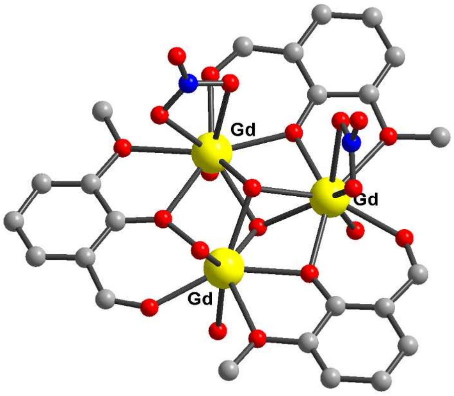


Figure 1. View of the trinuclear cation $[Gd_3(\mu_3\text{-OH})_2(o\text{-van})_3(O_2NO)_2(OH_2)_4]^{2+}$ (adapted from ref. 9).

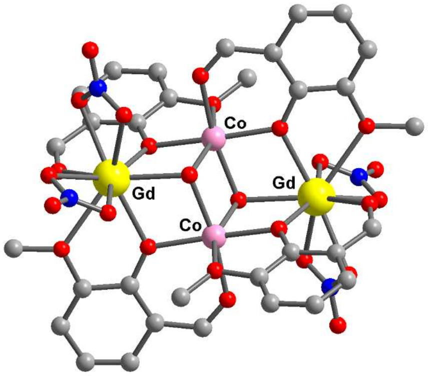


Figure 2. Crystal structure of $[(NO_3)_2Ln(o\text{-van})_2(\mu_3\text{-HO})Co_2(\mu_3\text{-OH})(o\text{-van})_2Ln(NO_3)_2]$ (adapted from ref. 15).

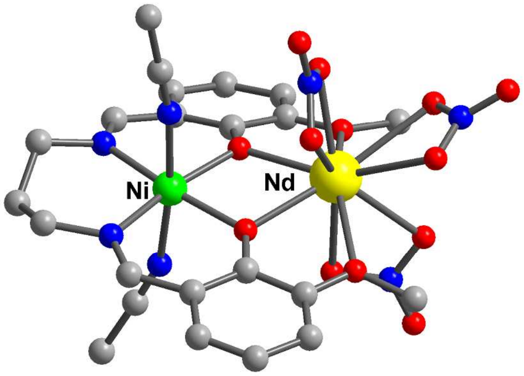


Figure 3. Crystal structure of $[Ni(CH_3CN)_2(valpn)Nd(O_2NO)_3]$ (adapted from ref. 16a).

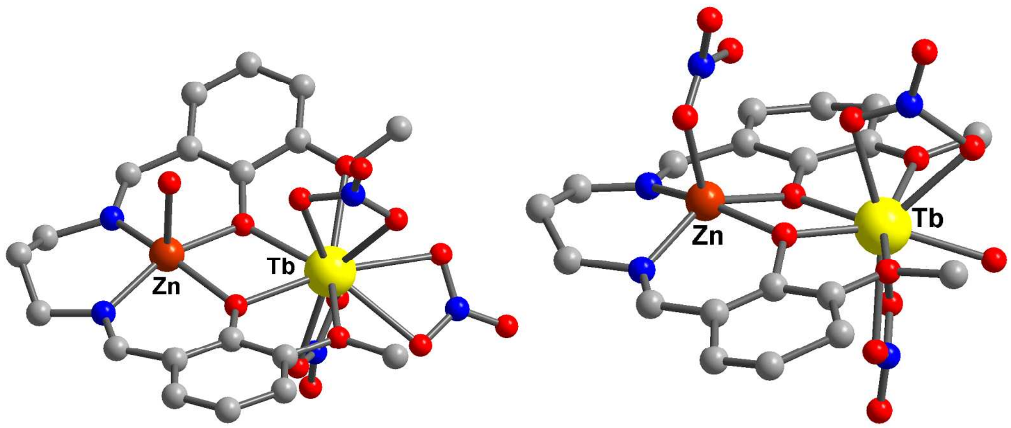


Figure 4. Crystal structures of [Zn(H_2O)(valpn)Tb(O_2NO)$_3$] and [Zn(ONO_2)(valpn)Tb(O_2NO)$_2$(H_2O)] (adapted from ref. 16b).

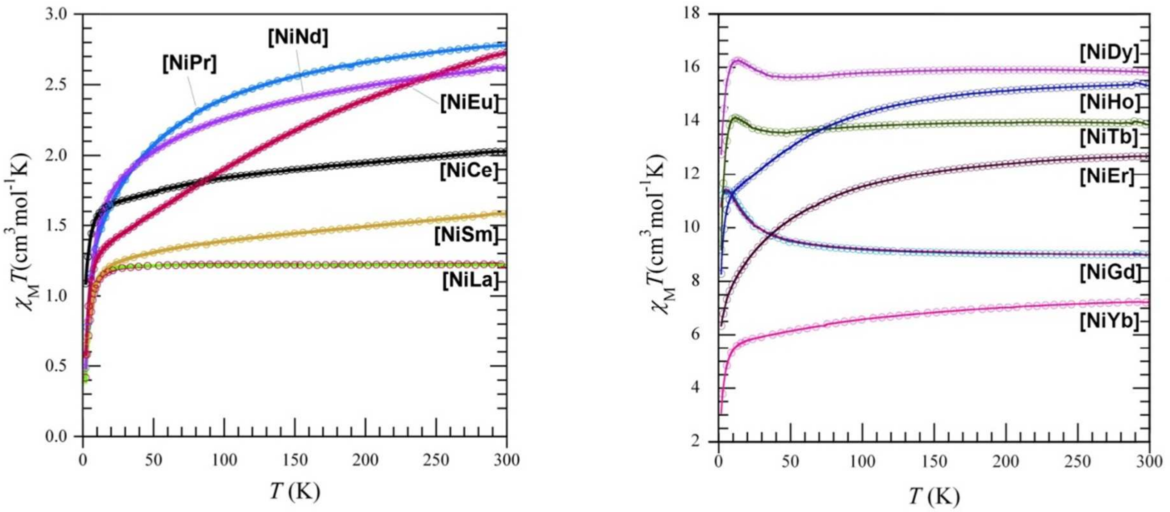


Figure 5. Magnetic properties ($\chi_M T$ vs T curves) of [NlLn] binuclear complexes (adapted from ref. 16a).

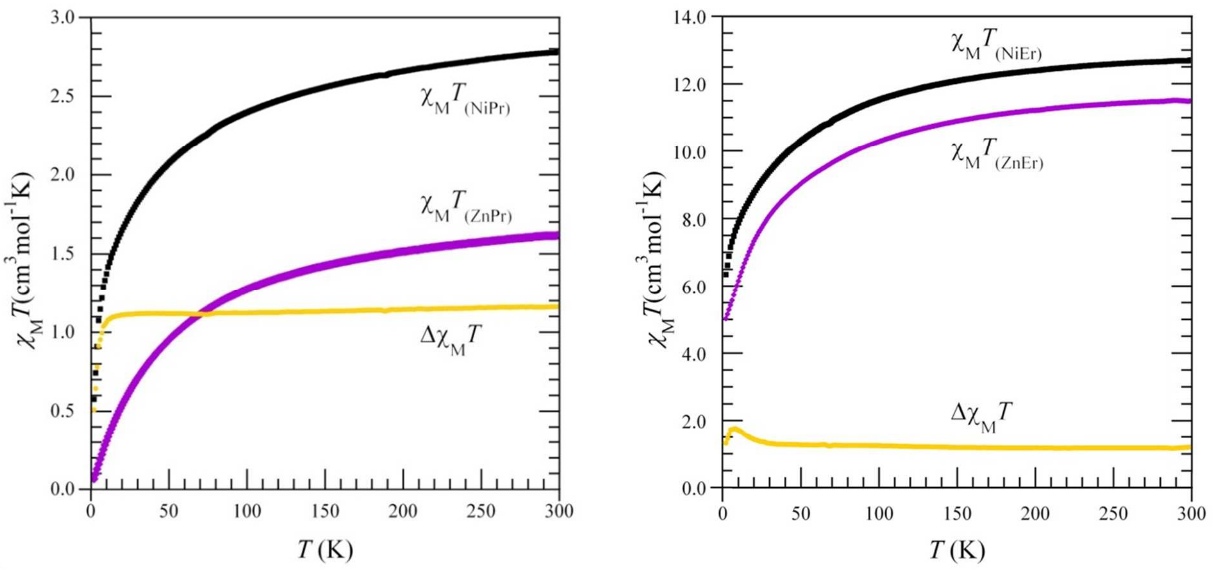


Figure 6. Temperature dependence of the difference $\Delta\chi_M T = \chi_M T_{(NiLn)} - \chi_M T_{(ZnLn)}$ (Ln = Pr, Er).

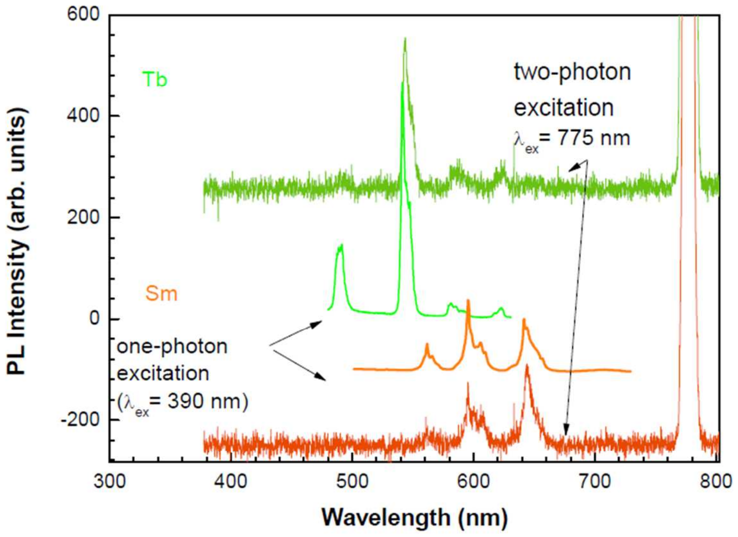


Figure 7. One and two-photon photoluminescence spectra for complexes $[Zn(H_2O)(Me_2valpn)Sm(O_2NO)_3]$ and $[Zn(H_2O)(Me_2valpn)Tb(O_2NO)_3]$.

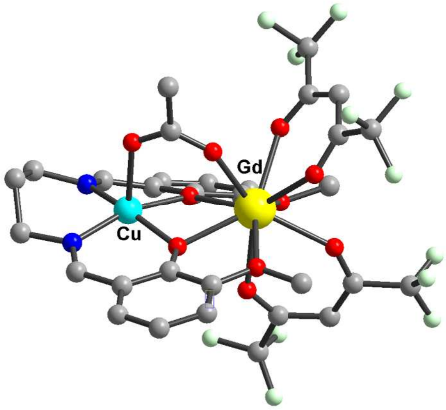


Figure 8. Crystal structure of the binuclear complex [Cu(valpn)(CH_3COO)Gd(hfac)$_2$] (adapted from ref. 20).

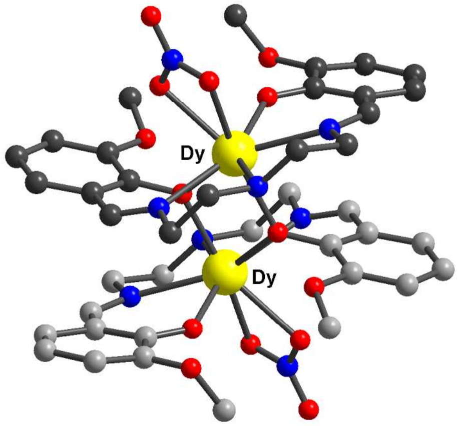


Figure 9. Perspective view of the binuclear complex [Dy$_2$(valdien)$_2$(NO_3)$_2$] (adapted from ref. 28b).

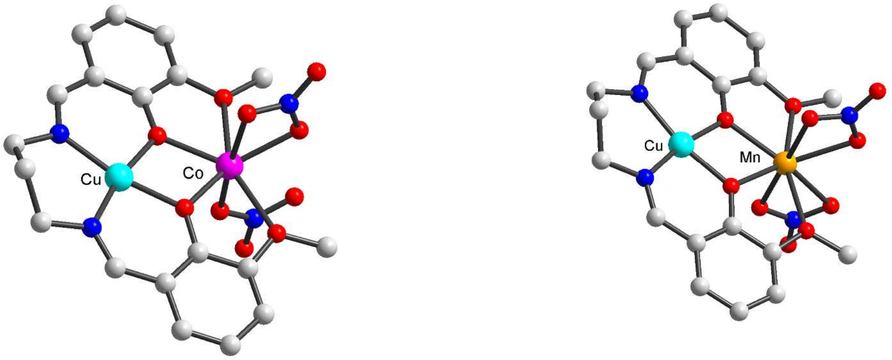


Figure 10. Crystal structures of [Cu(valpn)Co(O_2NO)(ONO_2)] and [Cu(valpn)Mn(O_2NO)$_2$] (adapted from ref. 30a).

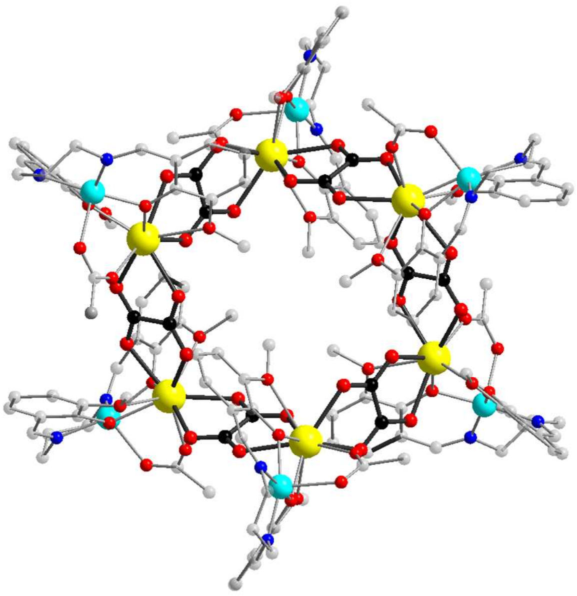
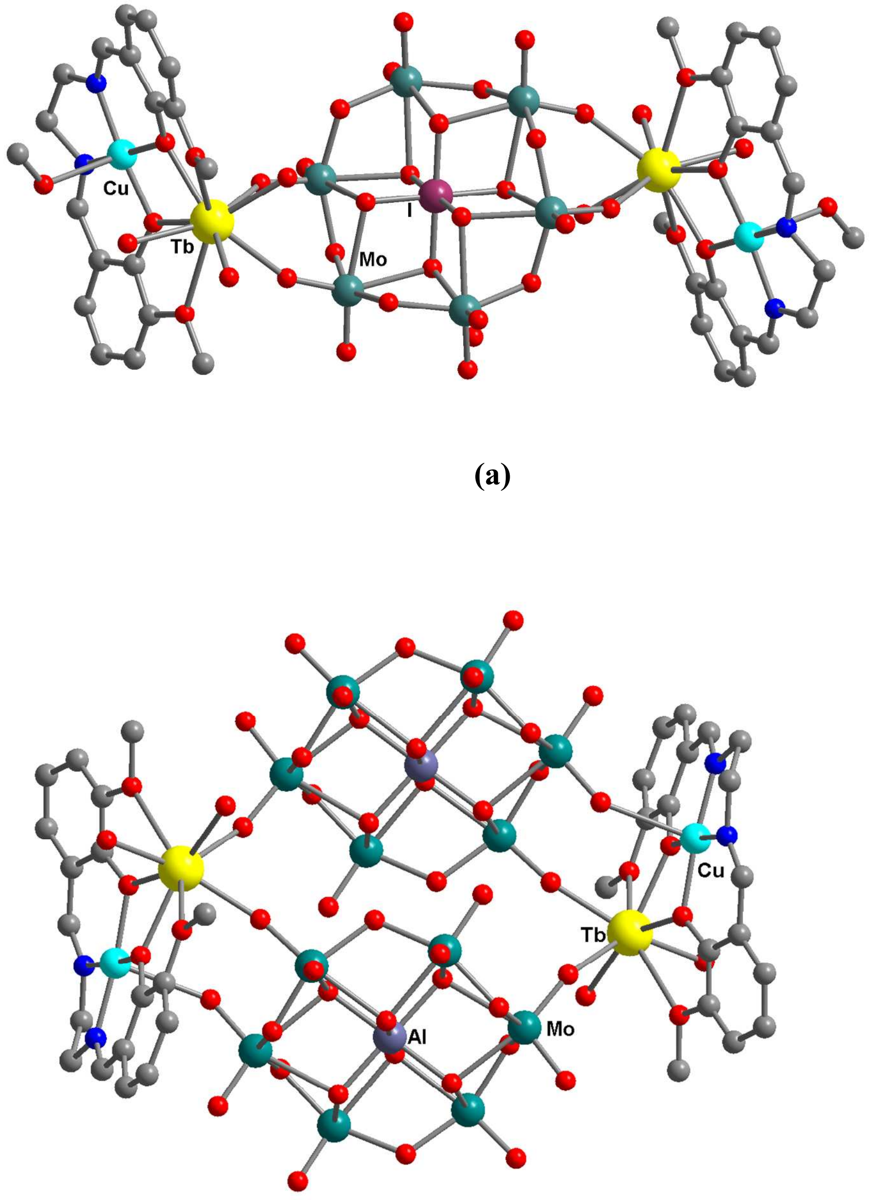


Figure 11. Crystal structure of the dodecanuclear cluster [{(valpn)Cu^{II}Dy^{III}(CH_3COO)}$_6$(C_2O_4)$_6$] (adapted from ref. 32).



(a)

(b)

Figure 12. Perspective views of: $[\{Cu(valen)Ln(H_2O)_3\}_2\{IMo_6O_{24}\}]Cl\cdot$(a) and $[\{Cu(valen)Tb(H_2O)_2\}_2\{AlMo_6O_{18}(OH)_6\}_2]$ (b) (adapted from ref. 33).

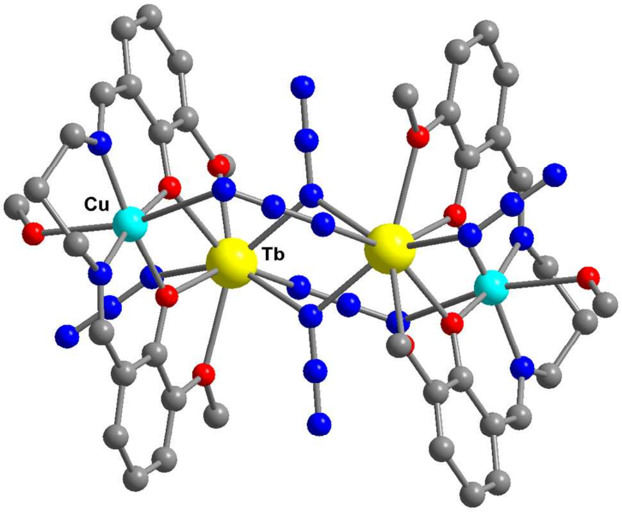


Figure 13. Crystal structure of [$Cu_2(valpn)_2Tb_2(N_3)_6$] (adapted from ref. 34).

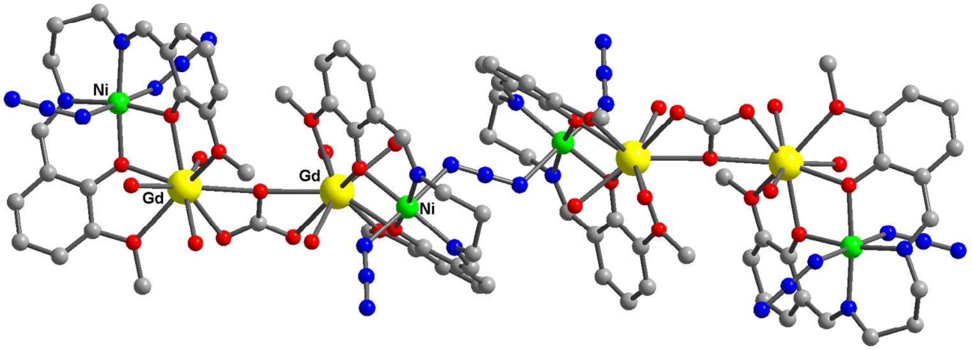


Figure 14. View of the octanuclear complex a [$(N_3)_{1.5}(H_2O)_{0.5}Ni(valpn)Gd(H_2O)_3(\mu$-$CO_3)Gd(H_2O)_3(valpn)Ni(N_3)(\mu_{1,3}$-$N_3)_{0.5}]_2](N_3)_2$ (adapted from ref. 36).

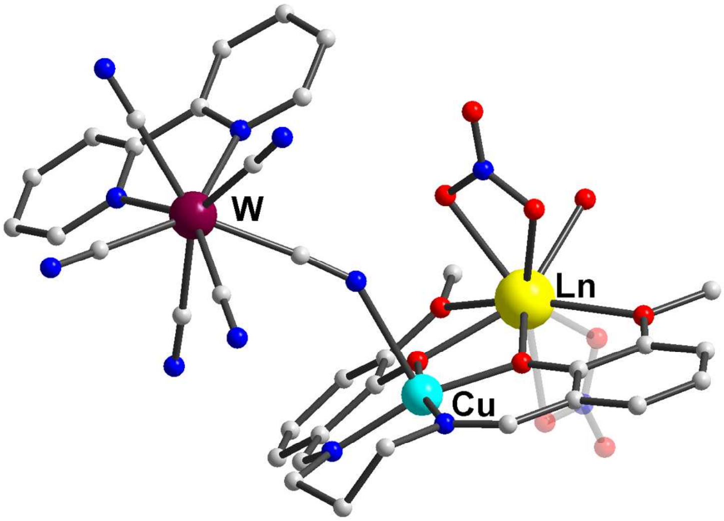


Figure 15. Crystal structure of the heterotrimetallic complexes [{(bipy)W(CN)$_6$}Cu(valpn)Ln((H$_2$O)(O$_2$NO)$_2$], Ln = Gd, Tb, Ho (adapted from ref. 37).

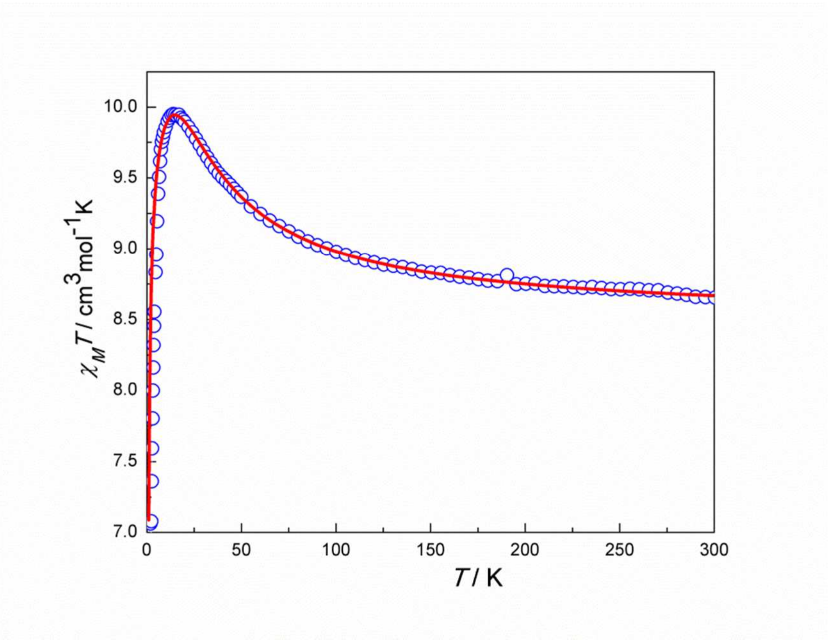
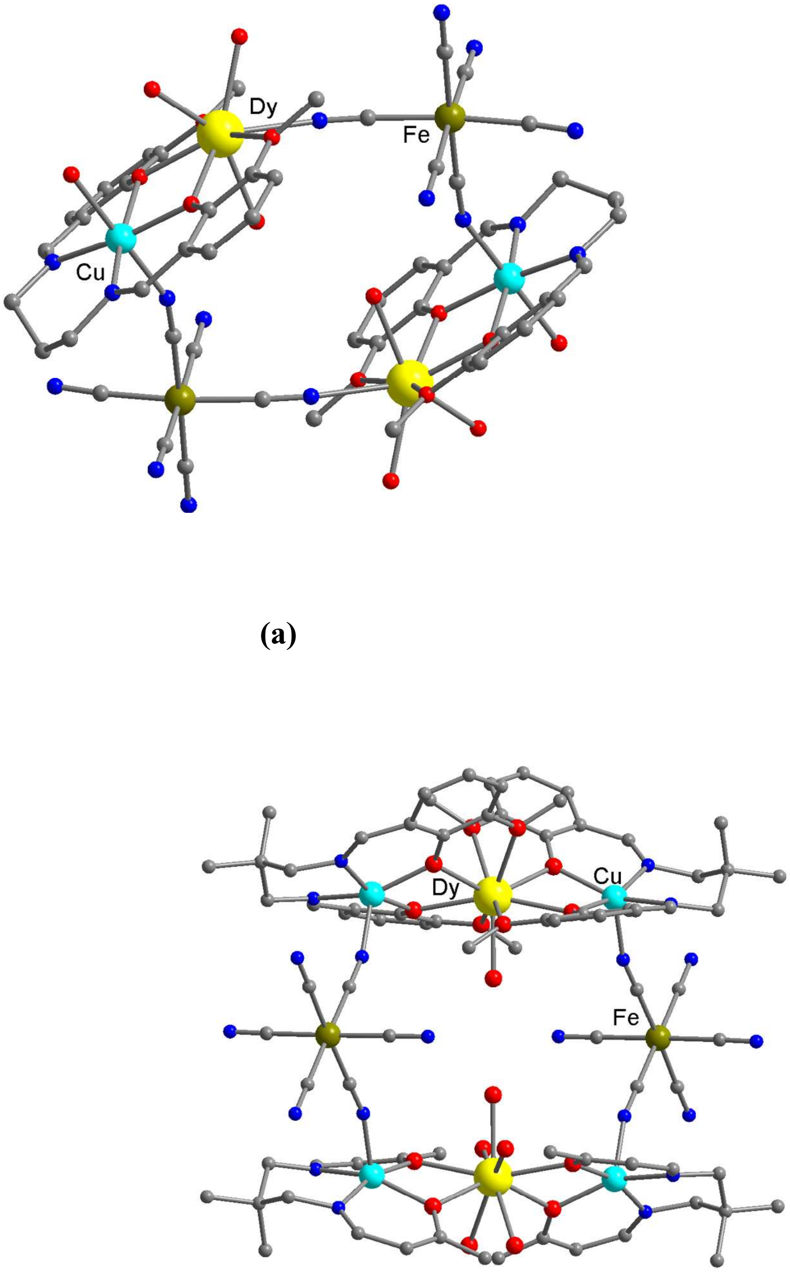


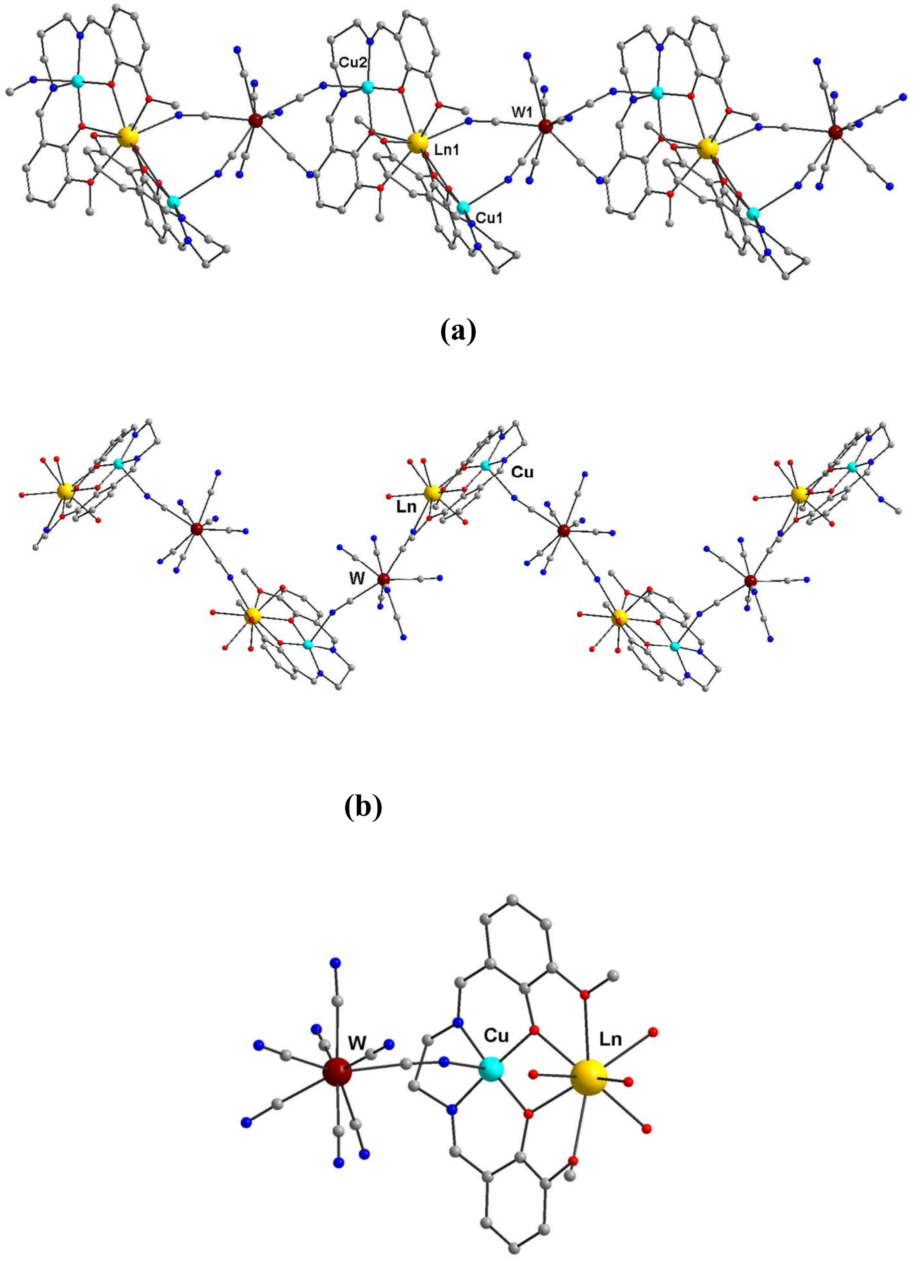
Figure 16. Temperature dependence of the $\chi_M T$ product for [{(bipy)W(CN)$_6$}Cu(valpn)Gd((H$_2$O)(O$_2$NO)$_2$].



(a)

(b)

Figure 17. Hetrotrimetallic $Cu^{II}Ln^{III}Fe^{III}$ clusters: $[Ni(valpn)(H_2O)Dy(H_2O)_3Fe(CN)_6]_2\cdot$(a); $[\{Ni(Me_2valpn)\}_2Dy(H_2O)Fe(CN)_6]_2$ (b) (adapted from ref. 39).



(a)

(b)

(c)

Figure 18. Heterotrimetallic $Cu^{II}Ln^{III}W^{V}$ chains (a, b,) and a trinuclear complex (c) obtained using $[W(CN)_8]^{3-}$ as a metalloligand (adapted from references 42 and 43).

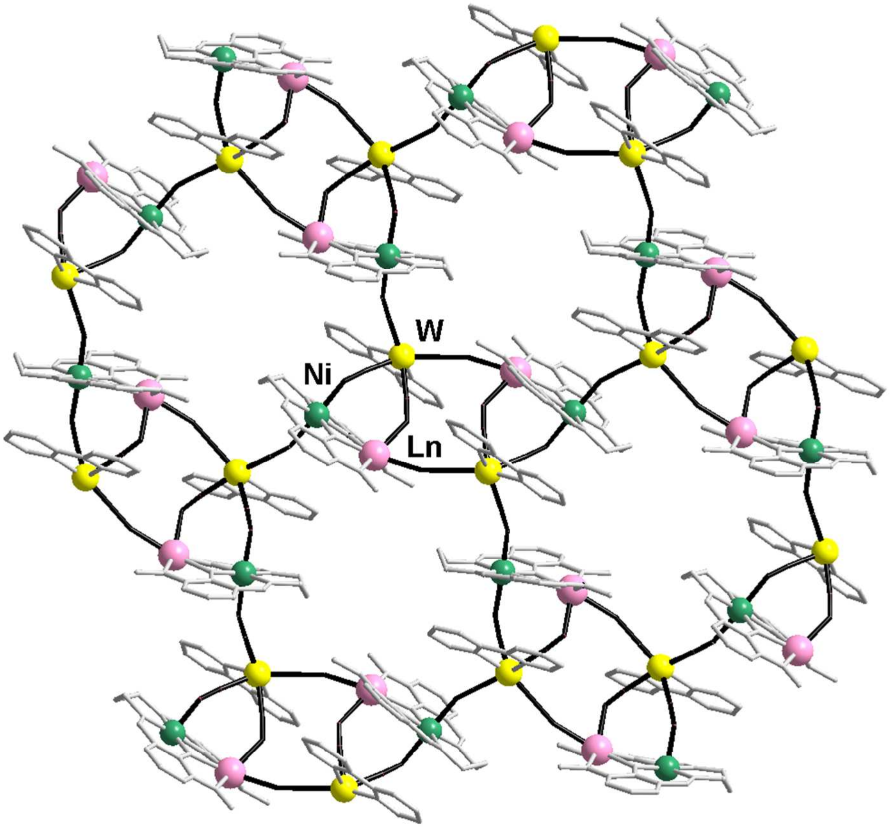


Figure 19. Heterotrimetallic $Ni^{II}Ln^{III}W^{V}$ 2-D coordination polymers: $\{[Ni^{II}(valpn)Ln^{III}(ONO_2)_2(H_2O)(\mu\text{-}NC)_3Fe^{III}(bipy)(CN)]_n$ Ln = Gd, Tb, and Dy (adapted from ref. 44).

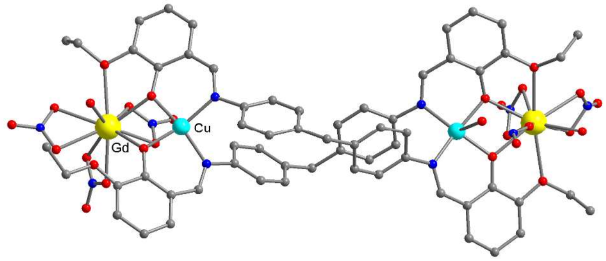


Figure 20. View of a double stranded helicate (adapted from ref. 46b).

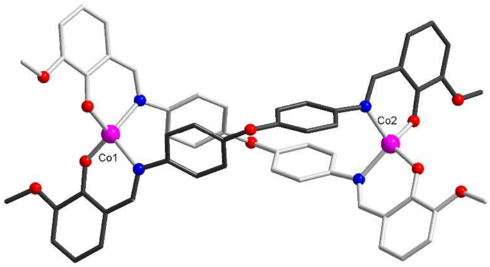
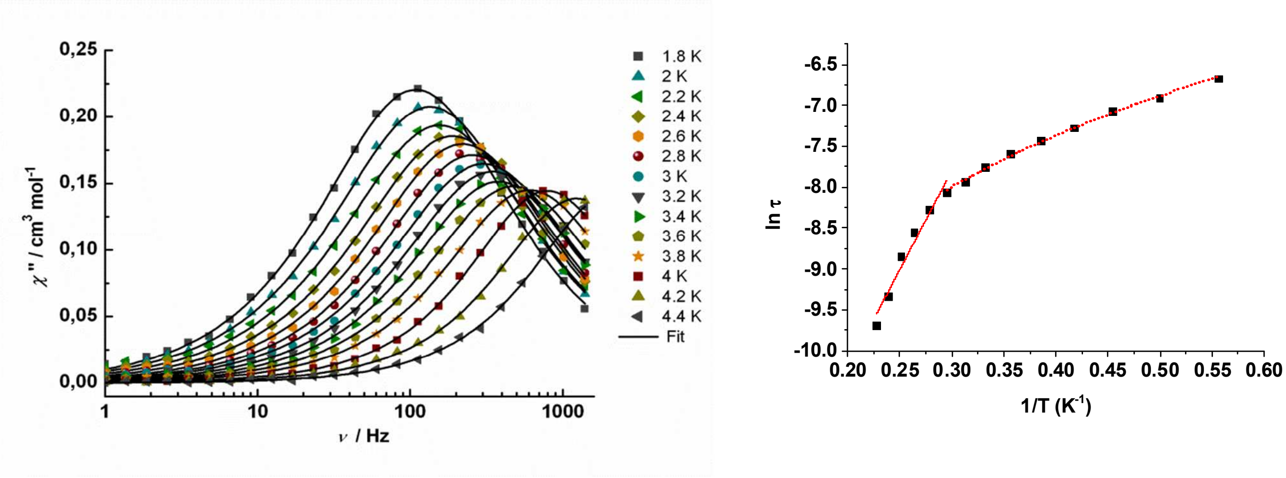


Figure 21. Perspective view of a double stranded binuclear cobalt(II) helicate (adapted from ref. 47).



(a) **(b)**

Figure 22. Frequency dependence of the out-of-phase ac susceptibility (a) and Arrhenius plot (b) for the cobalt helicate adapted from ref. 47).

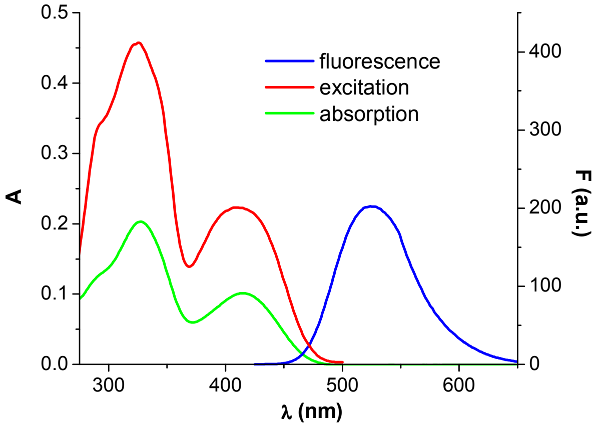


Figure 23. Absorption, excitation and fluorescence spectra of the binuclear zinc helicate in chloroform. $\lambda_{ex} = 416$ nm; $\lambda_{em} = 525$ nm.

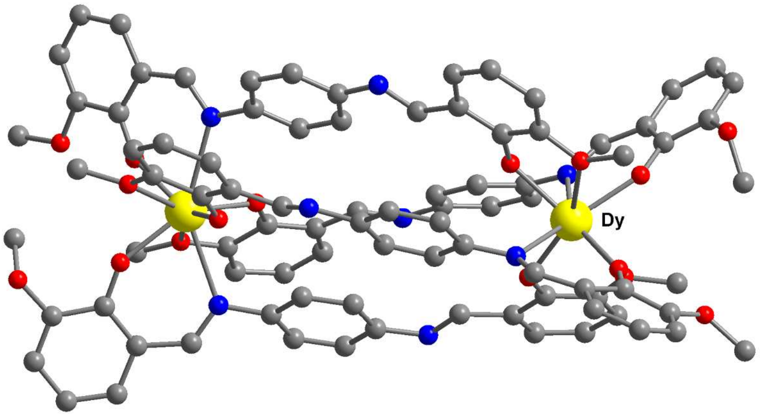


Figure 24. Perspective view of a quadruple stranded binuclear helicate (adapted from ref. 49.

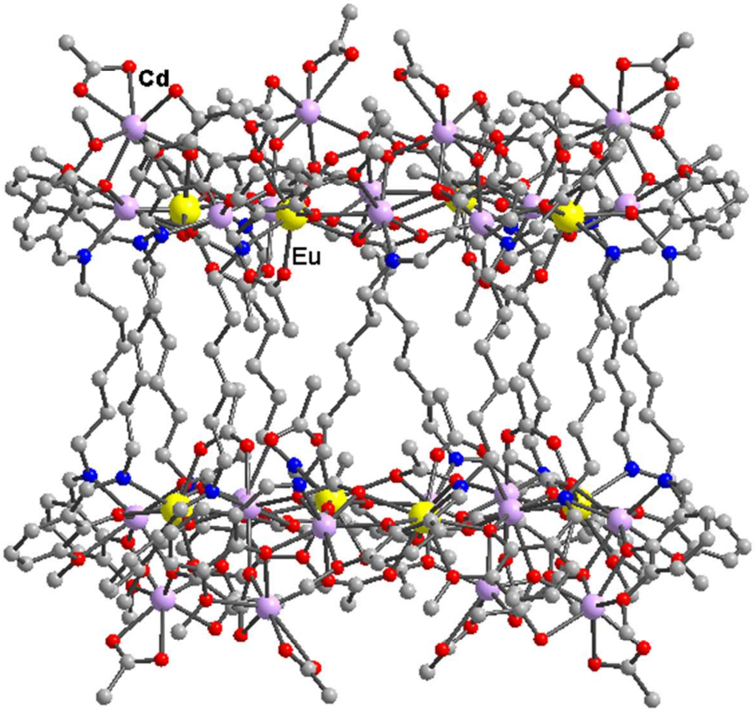


Figure 25. View of the drum-like cluster [Eu_8Cd_{24}] (adapted from ref. 51a).

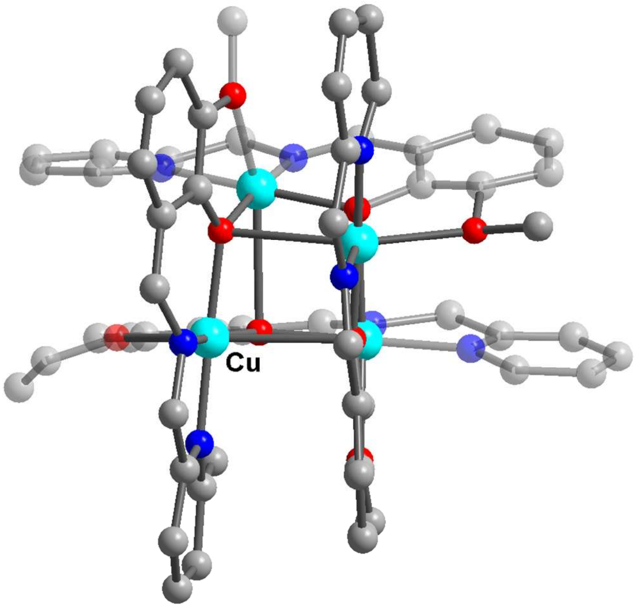


Figure 26. Crystal structure of the heterocubane cationic complex: [Cu(valampy)$_4$]$^{4+}$ (adapted from ref. 53).

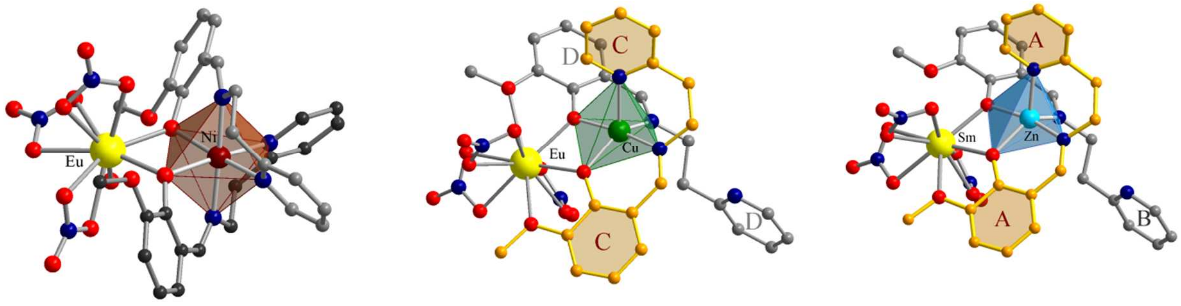


Figure 27. Crystal structures of three binuclear 3d4f complexes with valaepy^{2-} ligands: [Ni(valaepy)$_2$Eu(O$_2$NO)$_3$(H$_2$O)], [Cu(valaepy)$_2$Eu(O$_2$NO)$_3$], and [Zn(valaepy)$_2$Sm(O$_2$NO)$_3$] (adapted from ref. 54).

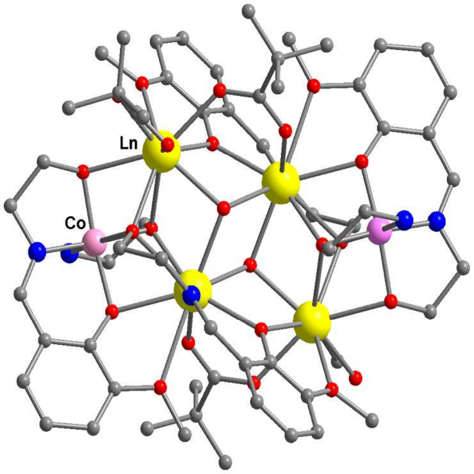
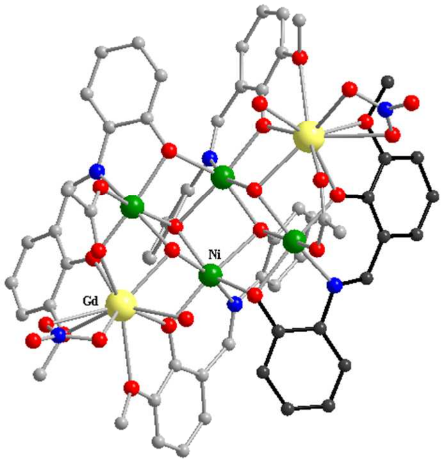
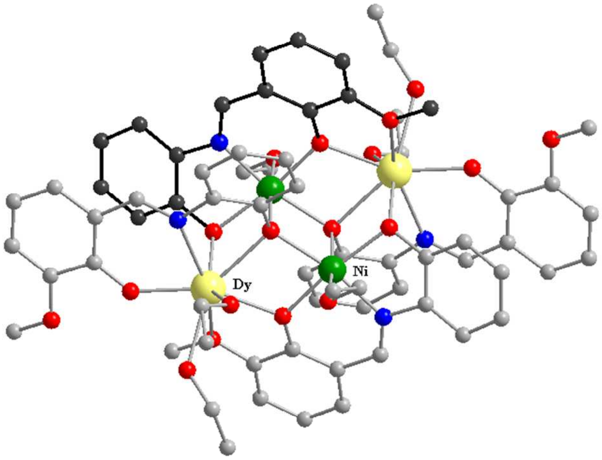


Figure 28. Crystal structure of [$Co_2Ln_4(\mu_3\text{-}OH)_2(piv)_4(valmea)_4(mea)_2$] complexes (adapted from ref. 60.



(a)



(b)

Figure 29. Crystal structures of [$Ni_4Dy_2(\mu_3\text{-}OH)_2(valamph)_4(CH_3COO)_2(NO_3)_2(H_2O)_2$] (a), and [$Ni_2Dy_2(valamph)_4(EtOH)_6$]$(ClO_4)_2$ (b) (adapted from references 62 and 63).

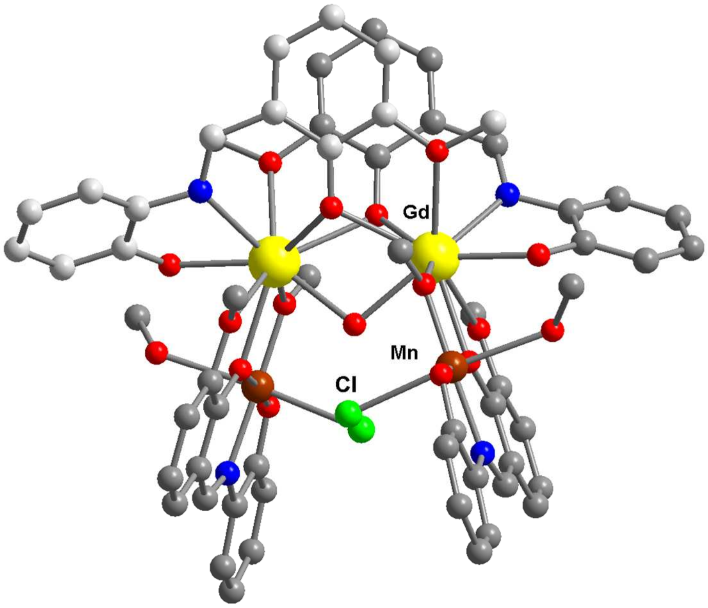
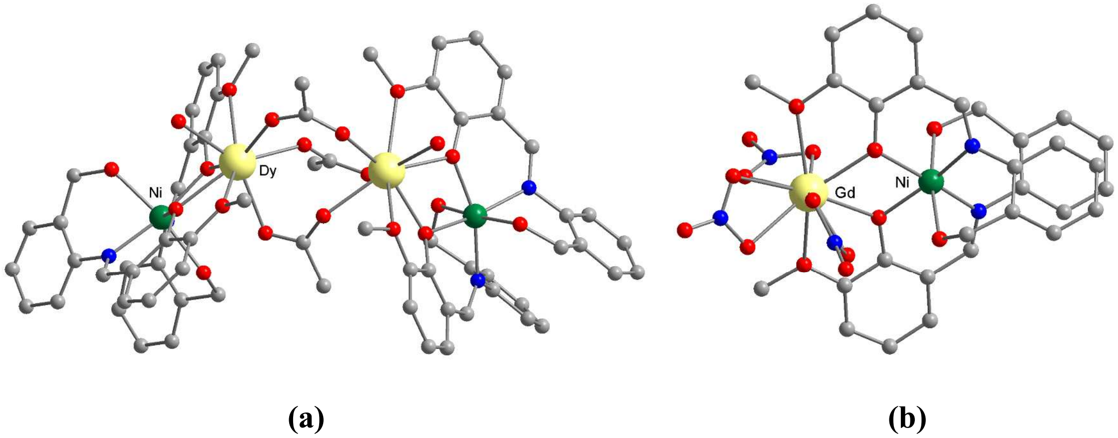


Figure 30. Crystal structure of the tetranuclear complex $[Mn^{III}_2Ln^{III}_2(O)(valamph)_4(CH_3OH)_4(Cl_2)]$ (adapted from ref. 65).



(a) (b)

Figure 31. Crystal structures of $[Ni^{II}_2Dy^{III}_2(CH_3COO)_3(Hvalabz)_4(H_2O)_2](NO_3)_3$ (a) and $[Ni^{II}Gd^{III}(Hvalabz)_2(NO_3)_3]$.(b) (adapted from ref. 66).

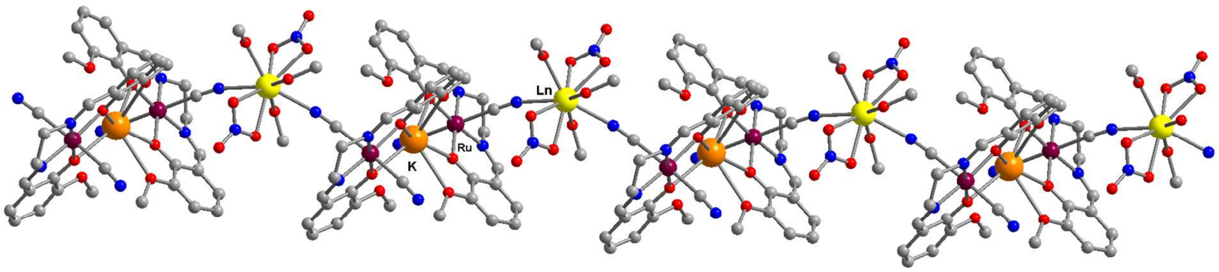
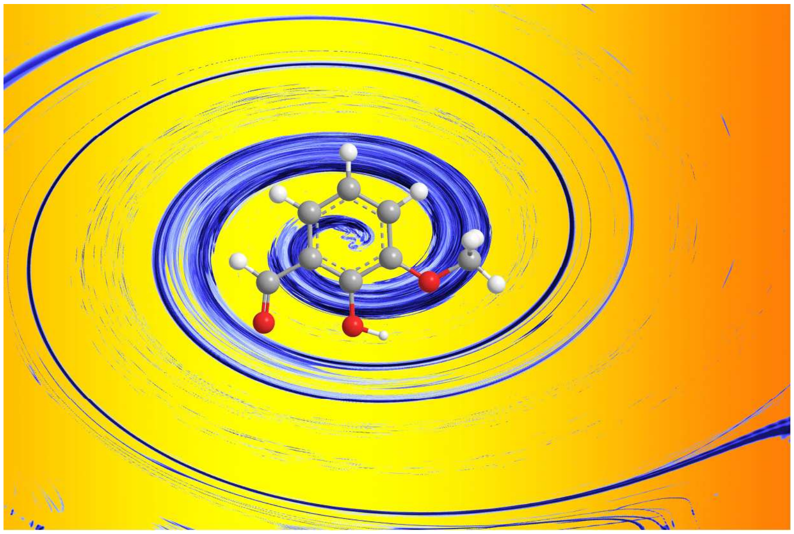


Figure 32. Crystal structure of the heterometallic chains $^{1}{}_{\infty}$[{Ru(valen)(CN)$_2$KRu(valen)(CN)$_2$}{Ln(O$_2$NO)$_2$(CH$_3$OH)$_3$}]·(Ln = Gd, Tb, Dy) (adapted from ref. 80).

TOC entry

Recent and relevant examples of homo- and heterometallic complexes generated by Schiff base ligands derived from *o*-vanillin, as well as their properties are discussed.



Biography

Marius Andruh (b. 1954) is Chair of the Inorganic Chemistry Department at the University of Bucharest and Professor in Coordination Chemistry. His major research interests are focused on metallosupramolecular chemistry, molecular magnetism and crystal engineering. He is a member of the Romanian Academy (2001), of the Academia Europaea (2004), and of the European Academy of Sciences (2010). He was a visiting Professor at several Universities (Bordeaux, Göttingen, Strasbourg, Toulouse, Angers, Manchester, Brno, Jena, Paris, Valencia, Niteroi-Rio de Janeiro).