Phenol-pyrazole ligands in the design of manganese(III) compounds : synthesis, structural characterization and study of the magnetic properties

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Chapter 1

Introduction*

The aim of the thesis is the synthesis of mainly manganese complexes with phenol-pyrazole ligands. The chapter starts with the goal and outline of the thesis. To justify the use of phenol-pyrazole ligands, this chapter concludes with an overview of the role of pyrazole-based ligands in the formation of transition-metal clusters. The ability of the pyrazole ligand to provide a pathway for magnetic exchange interactions is highlighted.

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1.1. Introduction

In the last decades, many efforts have been made to control matter at the molecular level, in a length scale range of 1–100 nm. Researchers have progressively developed, characterized and addressed new materials that can be used for technological applications, such as in medicine, electronics, catalysis, etc.[1] Two main approaches are taken to miniaturize the size of the materials, the first of which is the so-called "top-down" approach, which comes down to the fragmentation of already known materials. This approach is based on miniaturizing techniques, such as machining, templating or lithographic techniques.[2] The disadvantages are the lack of atomic-level control and the limitations of the size. The other approach is called the "bottom-up", which is based on self-assembly of molecular precursor building blocks into larger structures. The advantages are the lower costs as compared with the "top-down" approach and the good control to scale the dimensions.[3,4]

Materials reduced to the nanoscale can show new physical properties, associated with quantum effects, enabling unique applications.[3,5,6] One of these properties is associated with magnetism. In this sense, a new field entitled *molecular magnetism* has emerged in the last years.[3,5,6] This is an interdisciplinary field, where chemists design and synthesize new magnetic molecules and physicists develop techniques to understand in more detail their novel magnetic properties.[7] The key property of a bulk magnet is that, below a critical, magnetic ordering temperature, T_C, it exhibits spontaneous magnetization. It means that it remains magnetized after the removal of magnetic field. Molecule-based magnets, *i.e.* magnets made from molecules, constitute a broad emerging class of new materials that extend the properties typically associated with magnets to include some advantages such as low-density, transparency, electrical insulation, solubility, biocompatibility and the possibility of low-temperature fabrication.[3,5,6]

The origin of the magnetic moments in molecular magnetic materials, just as in bulk, is the unpaired electrons of transition-metal ions, rare-earth ions or organic radicals of which the molecules are composed. Transition-metal ions and rare-earth ions require a magnetic or diamagnetic ligand to be stabilized in a molecular unit. Therefore, the magnetic properties of molecular polymetallic systems derive from the intramolecular exchange interactions between the paramagnetic metal ions through the bridging ligands. In particular, to design polymetallic clusters, small ligands are necessary to provide efficient bridges and to determine the growth of the cluster. Often these ligands are monoatomic ligands, such as O^{2-}, S^{2-}, F^{-}, *etc.*, or ligands with a single donor atom, like OH^{-}, OR^{-}, which are known to transmit the magnetic interactions effectively. In addition, blocking or terminal ligands are required to prevent the growth of the cluster and to avoid the formation of polymeric structures.

Two strategies for the synthesis of polymetallic clusters have been largely developed depending on the choice of the polydentate ligand. One strategy is just serendipity, in which flexible ligands are used, such as pyridonate[8] or carboxylate ligands,[9] which have been the most studied bridging ligands. The identity of the final products is very difficult to predict, because of the large variety of orientations and binding modes of the ligand that impose little or no geometric effect.[10] The other strategy is based on a more rational design that can be performed by using rigid ligands, such as cyanide,[11] or polytopic picolinic-hydrazone ligands.[12] In the latter case, the ligand imposes the geometry of the cluster and the results are more predictable.[13,14] Synthetic strategies involve the use of preformed simple molecules, *i.e.* building blocks with a tendency of self-assembly to form more complex molecules. Some examples of building blocks are hexacyanidometalates,[15-17] trinuclear manganese complexes,[9] or mononuclear manganese(III) salen complexes.[18]

In the design of polymetallic clusters, parameters like the pH of the solution, the solvent or the metal to ligand ratio, can also determine the variety of products. However, the choice of a suitable polydentate ligand remains essential, since two requirements need to be fulfilled: the ability to bridge more than one metal ion and to provide a suitable intramolecular pathway for magnetic exchange interactions.

1.2. Aim of this thesis

The purpose of this thesis research is to develop new synthetic strategies to obtain molecular-based magnetic materials, exploring the coordination chemistry of phenol-pyrazole ligands as bridging ligands. Carboxylates and Schiff-base derivative ligands are widely studied for the formation of polymetallic complexes.[9,18] However, the synthesis of polymetallic clusters containing new ligands is still rather limited. Many pyrazole-based ligands have the ability to bridge two metal ions and to provide an effective magnetic-exchange pathway between them. The chemistry and the magnetic properties of dinuclear pyrazolate compounds are well understood.[19-22] However, the research focused on polynuclear compounds,[23,24] especially dealing with high-nuclearity clusters is still developing.[25] Variations in the substituents on the pyrazole ring can control the distances between the metal ions and the electronic and magnetic properties. Therefore, a phenol moiety has been introduced as a substituent on the pyrazole ring to increase the number of possible coordination sites. Only a few examples of polymetallic clusters have been reported until now with phenol-pyrazole ligands and most of them have been obtained in the course of this thesis project.[26-31] Following earlier promising results in our group,[30,32] a family of phenol-pyrazole ligands has been synthesized with the main difference on the substituent in the fifth position of the pyrazole group (Figure 1.1).

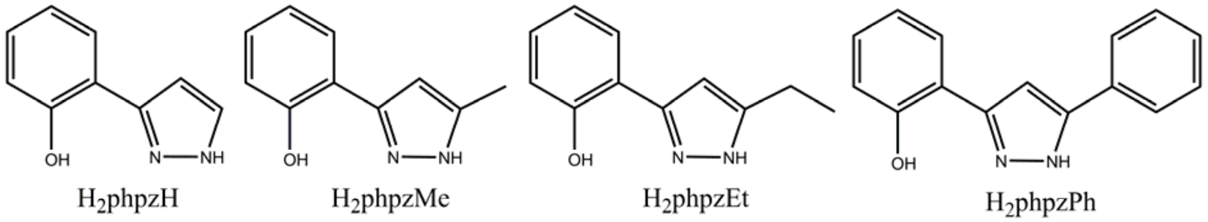


Figure 1.1. Phenol-pyrazole ligands (H_2phpzR; R = H, Me, Et, Ph) employed in this thesis.

The ligand is crucial in the organization of the paramagnetic metal ion. Nevertheless, the choice of the magnetic carrier is essential, since the origin of the magnetic moment resides in the electrons. In this thesis project, the manganese metal ion has been chosen to explore its coordination chemistry, because of some special advantages. Manganese displays a large variation in oxidation states, *e.g.* manganese(II) (d^5), manganese(III) (d^4) and manganese(IV) (d^3) for the formation of complexes. Most of these types of manganese cations behave as a hard Lewis acid. So they are well stabilized by O-donor ligands. In most of the manganese complexes, the manganese(II) and manganese(III) ions are high-spin with a large number of unpaired electrons.[33] Besides the paramagnetic nature of the manganese ion in various oxidation states, another crucial characteristic is the negative Ising type of anisotropy that the manganese(III) ion displays due to the Jahn-Teller distortion, which can provide additional interesting magnetic properties.[7,34]

In the following section of the present chapter, the choice of phenol-pyrazole ligands in this thesis as bridging ligands is justified with an overview of polynuclear metallic clusters containing pyrazole-based ligands.

In Chapter 2, the synthesis and the magnetic and thermal properties are presented of a family of mononuclear manganese(III) compounds with the general formula $[Mn(HphpzR)_2X]$ (R = H, Me, Et, Ph; $X^- = Cl^-$, Br^-). The influence of the type of ligand is reflected in the crystal packing and the magnetic properties of the compounds.[35]

Chapter 3 deals with the use of some of the mononuclear compounds presented in Chapter 2 as building blocks to form trinuclear manganese(III) compounds with the $[Mn_3(\mu_3\text{-}O)(phpzR)_3]^+$ core. The chapter contains a study of the magneto-structural correlations of all the oxide-centred trinuclear manganese(III) compounds reported in the literature.[36] In Chapter 4, the impact of the co-ligands on the trinuclear compounds with the core $[Mn_3(\mu_3\text{-}O)(phpzR)_3]^+$ is described.[37]

Chapter 5 is devoted to some high-nuclearity manganese(III) clusters. The formation and the stability of the core and the magnetic properties depending on the type of phenol-pyrazole ligands and the reaction conditions are discussed.

Chapter 6 describes the coordination versatility of H_2phpzMe ligand with transition-metal ions other than the manganese(III) ion.[38]

Chapter 7 presents the summary and conclusions of this work, as well as some future prospects.

In Appendix A, HFEPR studies are described, dealing with two mononuclear manganese(III) compounds presented in Chapter 2 to determine the sign and magnitude of the zero-field splitting parameters. In Appendix B, crystallographic data of the compounds presented in Chapter 5 is reported.

Parts of this thesis have been published (Chapter 2, 3, 4 and 6),[35-38] or will be submitted for publication (Chapter 1 and Chapter 5).

1.3. Coordination versatility of pyrazole-based ligands towards high-nuclearity transition-metal clusters

1.3.1. Introduction

The choice of the bridging ligand is crucial in the formation of polynuclear cluster compounds. In this thesis, phenol-pyrazole ligands have been chosen because as had been established with numerous polynuclear compounds,[23,24] pyrazole ligands fulfil both conditions, they can bridge more than one metal ion and they provide a suitable intramolecular pathway for magnetic exchange interactions. In the present section, the coordination versatility of pyrazole-based ligands towards the formation of polymetallic compounds,[25] especially dealing with high-nuclearity clusters is illustrated.

1.3.2. Pyrazole

Pyrazoles are five-membered heterocyclic aromatic rings consisting of three carbon atoms and two nitrogen atoms at the positions 1 and 2 (Figure 1.2). The N(1)–H has an acid character due to the proton, whereas the N(2) has a basic lone pair in the sp^2 orbital. Therefore a basic character is present. Tautomerism exists in the case of symmetrical substitution, or non-substitution on the ring, unless the substituent is in position 1, because the rupture of the N–C bond is more difficult than that of the N–H bond. Five-membered heterocycles, such as pyrazoles, are π-excessive. As a consequence they are poorer π-acceptor and better π-donors than six-membered heterocycles. Hence, they can act as a hard donor site.[39,40] Numerous synthetic routes have been used to obtain pyrazole-based ligands. However, two routes are the most important: the condensation of a 1,3-diketone (1,3-dicarbonyl) with hydrazine derivatives and the 1,3-dipolar cycloaddition of diazoalkane with alkynes.[41]

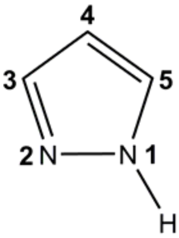


Figure 1.2. Pyrazole (Hpz).

Pyrazoles can behave either as monodentate or as bidentate ligands, after deprotonation of the N(1)–H group. The pyrazolato anion can act as an endo- (η^2), or an exo-bidentate (η^1–η^1) bridging ligand in the form of the pyrazolato anion (Figure 1.3). This coordination ability or nucleophilicity is controlled by the nature of the metal ion and the substituents on the pyrazole ring. Substituents at the 3- and 5-positions modify the steric properties, whereas substituents at the 4-position, can mainly change the electronic properties.

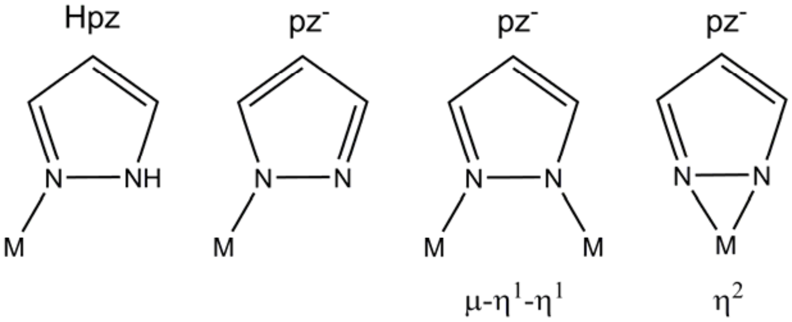


Figure 1.3. Common coordination modes of the pyrazole ligand and the corresponding anionic ligand.

The study of the coordination chemistry with pyrazole ligands began in 1889 with the report of a silver pyrazole complex, $[Ag(pz)]_n$.[42] Much later, Trofimenko *et al.* stimulated the research with the introduction of poly(pyrazolyl)borate chelating ligands in coordination chemistry.[43-46] After this discovery, numerous papers and reviews have been written illustrating the rich coordination chemistry of pyrazole-based ligands.[39,40,47-50] In the literature, three main reviews have been reported dealing with polynuclear compounds[23-25]. The first review was published in 1997 illustrating the catalytic activity of polynuclear heteroatom-bridged pyrazole complexes.[24] Two other reviews have appeared more recently.[23,25] One of them deals with di-, oligo- and polynuclear transition-metal complexes with substituted pyrazole ligands having chelating side arms.[23] The other review describes metal-cluster compounds with pyrazole-based ligands.[25]

1.3.3. Clusters with pyrazole-based ligands

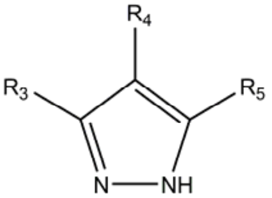
1.3.3.1. Introduction

In this section, the aim is to provide an overview of the pyrazole-based ligands used to form transition-metal clusters. In addition, the ability of pyrazole to provide a pathway for magnetic exchange interactions is highlighted. Only in the last decade, a significant development has been achieved in the coordination chemistry with pyrazole ligands to form polymetallic clusters. Three main reviews dealing with polynuclear complexes have already appeared.[23-25] Hence, pyrazoles substituted at *N*1 position, polymers and dinuclear compounds are not discussed.

As described above, the pyrazole and the pyrazolato anion have numerous coordination modes, providing versatile coordination chemistry. The most common modes are shown in Figure 1.3. Deprotonated pyrazoles can link two metal ions resulting in a metal-metal distance between 3.5–4.5 Å. Changes in the substituents of the pyrazole ring can induce changes in the intermetallic distances, hence controlling the magnetic exchange interactions. Therefore, the compounds discussed in this text are grouped depending on the type of substituents in the pyrazole ligand.

1.3.3.2. Pyrazole ligands with non-coordinating substituents

A significant number of cluster compounds containing pyrazole ligands has been obtained to date.[25] Most of the cluster compounds incorporate the pyrazole ligand or the pyrazole ligand with non-coordinating substituents, such as Br, NO_2, Me, Mes (2,4,6-trimethylphenyl), *etc.* in the 3-, 4-, or 5-position of the pyrazole ring (HR-pz). In this section, a summary is presented of these cluster compounds reported in the literature. Figure 1.4 shows some of the pyrazole ligands discussed in this section.



Ligand	R_3	R_4	R_5	Ligand	R_3	R_4	R_5	Ligand	R_3	R_4	R_5
HL1a	H	H	H	HL1e	H	I	H	HL1i	H	H	^{t}Bu
HL1b	H	Me	H	HL1f	H	NO_2	H	HL1j	H	H	4-F-Ph
HL1c	H	Cl	H	HL1g	H	CHO	H	HL1k	Me	H	Me
HL1d	H	Br	H	HL1h	H	H	Mes	HL1l	CF_3	H	CF_3

Figure 1.4. Some of the discussed pyrazole ligands with non-coordinating substituents.

Trinuclear complexes are the most common clusters with pyrazole ligands or pyrazole derivatives containing non-coordinating substituents, in which the compound can adopt two different types of structure. The first type is a linear structure which can be formed when the pyrazole is deprotonated and it bridges the metal ions as shown in Figure 1.5a, whereas other ligands are found at the terminal positions, *i.e.* halogens, acetylacetonate, non-deprotonated pyrazoles or cyclopentadienyl ligands. Some examples are reported with nickel(II),[51,52] cobalt(II),[53,54] palladium(II) ions,[54] and palladium(II)/cobalt(II) mixtures.[54] Weak antiferromagnetic interactions are observed between the paramagnetic metal ions in all the cases.

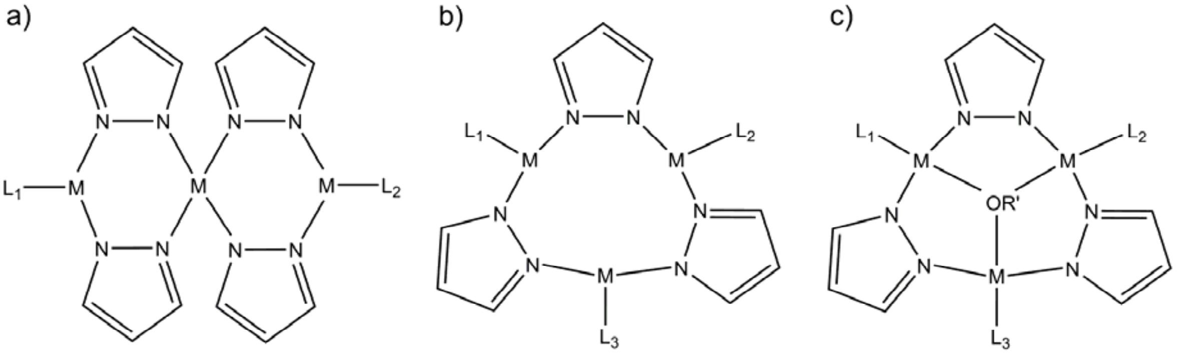


Figure 1.5. Trinuclear types of pyrazole-bridged compounds.

The second possible type of structure that trinuclear compounds can adopt is the triangle, in which the transition-metal ions are at the vertexes of a triangle (Figure 1.5b,c). Monovalent group 11 ions (copper(I), silver(I) and gold(I)) and mercury(II) ions form compounds with a general formula $[M(R\text{-}pz)]_3$ (Figure 1.5b).[55-62] In some cases, the distance between the trinuclear units is small, forming dimers of trimers.[63-66] Luminescence properties were studied in some of this type of complexes.[61,67] Trinuclear heterobimetallic gold(I)-silver(I) compounds have been synthesized with 3,5-diphenylpyrazole and other type of bridging ligands.[68,69] Compounds with the general formula $[M_3(R\text{-}pz)_6]$ are formed with divalent metal ions, *i.e.*, palladium(II),[70] platinum(II)[71] or platinum(II/III) ions.[71]

$[M_3\text{-}\mu_3\text{-}O(R')]^{m+}$ (R' = H, Me, m = 4, 5, 7) centred triangles have been reported with several transition-metal ions, such as iron(III), cobalt(II/III) and copper(II) ions (Figure 1.5c). The compound $X_4[Fe_3(\mu_3\text{-}O)(L1f)_6Cl_3]Cl_2$ ($X^+ = HNEt_3^+$, Bu_4N^+, PPh_4^+) has a structure which resembles the basic carboxylates because of the presence of six pyrazole ligands.[72] Mössbauer spectra, magnetic susceptibility and EPR studies have revealed the presence of antiferromagnetic interactions between the iron(III) ions and the achievement of a ground state of $S_T = 1/2$. In this case, the pyrazole ligands mediate stronger antiferromagnetic interactions than the analogous carboxylates.[72] Another example is $[Co_3(\mu_3\text{-}OH)(L1a)_4(dbm)_3]\cdot 2THF$ (Hdbm = dibenzoylmethane) that is a mixed-valence cobalt(II/III) compound with a μ_3-hydroxide bridge for which catalytic activity in the oxidation of the hydrocarbons has been reported.[73] Numerous compounds have been synthesized with copper(II) ion. Many of them have been reported by Raptis and co-workers,[74-80] who have studied the influence of non-coordinating substituents on the pyrazole ring and of the terminal ligands, L, present in the triangle. The general formula of these complexes is $[Cu_3(\mu_3\text{-OR'})(R\text{-pz})_3L_3]^{m+}$ (R' = H, Me; L = Cl^-, Br^-, Hpz, RCO_2^-, HL1g , H_2O, EtOH; R-pz$^-$ = L1a$^-$, L1f$^-$, L1h$^-$ and m = 0, 1, 2).[74-89] Most of the trinuclear centred copper(II) triangles are synthesized from a copper(II) salt and the pyrazole ligand in a molar ratio 1/1 or 1/2 in the presence of base and using different counter ions.[74] Other possible synthetic routes are: the substitution of the terminal ligand, L, or the centred anion, in a preformed trinuclear compound, or the addition of a bridging ligand such as carboxylate, an acid, a base or NaBr.[74,77,78,81,83] The control of the pH is crucial in the formation of new triangles, since numerous species often exist in solution. In some cases, compounds of higher nuclearity, or even polymers are obtained, in which the trinuclear structure can be retained.[79,81-85] Another synthetic route to obtain trinuclear-centred copper(II) compounds is by oxidation of mononuclear copper(I) complexes.[86] Apparently, the introduction of substituents in the 4-position of the aromatic ring does not affect the formation of trinuclear copper(II) complexes. However, the use of 3,5-substituted pyrazoles precludes the formation of the triangle, because of the steric effects of such side groups in the ligand. In these cases, mononuclear or dinuclear copper(II) complexes are obtained.[77,82] So far in only one case with substituents at the 3,5-positions, the trinuclear structure is retained.[87] Following similar procedures as those described for the synthesis of O(R')-centred copper(II) triangles (R' = H, Me), but with different amounts of the counter ion, the formation of new compounds with the formula $[Cu_3(\mu_3\text{-X})_2(R\text{-pz})_3X_3]^{2-}$ (X^- = Cl^-, Br^- and R-pz$^-$ = L1a$^-$–L1f$^-$) can be achieved (Figure 1.6).[74-77,79] Trinuclear copper(II) compounds with two types of bridging ligands, such as hydroxide and chloride ligands for $[Cu_3(\mu_3\text{-OH})(\mu\text{-Cl})Cl(L1a)_3(HL1a)_2]$,[90] and oxide and perchlorate ligands for $[Cu_3(\mu_3\text{-O})(L1a)_3(HL1a)_3(\mu_1,\mu_2\text{-ClO}_4)]\cdot CH_3OH$,[91] have also been reported.

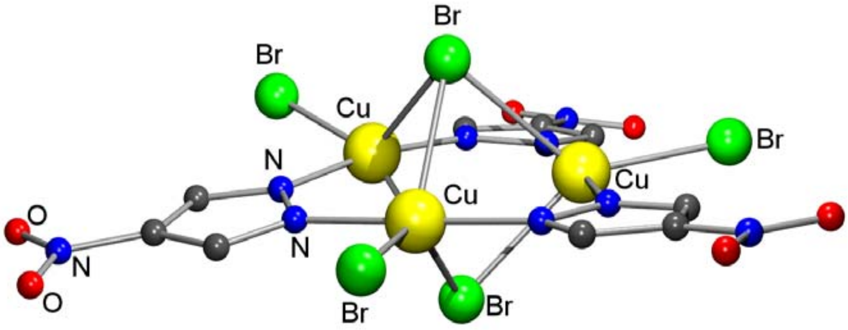


Figure 1.6. Molecular structure of the anion $[Cu_3(\mu_3\text{-Br})_2(L1f)_3Br_3]^{2-}$.[75]

The introduction of substituents on the pyrazole ring does not induce any significant structural differences, such as Cu···Cu distances or Cu–μ_3-O(R') (R' = H, Me) distances in the trinuclear copper(II) core. The main difference is the distortion of the Cu–μ-Y–Cu angle from going to μ-O^{2-}, OH^-, μ-X (X^- = Cl^-, Br^-). Magnetic susceptibility and EPR studies have been performed for some of the compounds (Table 1.1). Strong antiferromagnetic interactions between the copper(II) ions are operative in the case of the compounds with a Cu–μ_3-Y–Cu angle of *ca.* 120º (Y^{2-} = O^{2-}). Apparently, a decrease in magnitude of the antiferromagnetic exchange interaction is observed when the Cu–μ_3-Y–Cu angle decreases (Y^- = OH^-) and ferromagnetic interactions become operative when the Cu–μ_3-Y–Cu angle is *ca.* 80º (Y^- = Cl^-, Br^-). This change of the magnetic behaviour can be explained by the principles of the orbital complementarity and overlapping.[75] Small values of the magnetic susceptibility at low temperature are common in O(R)-centred copper(II) triangles.[87,90] This phenomenon can be described by the presence of antisymmetric exchange between the copper(II) ions in view of the magnetic susceptibility and EPR studies.[87]

Electrochemical studies have been performed for the compounds containing the core $[Cu_3(\mu_3\text{-}O(R'))(R\text{-}pz)_3L_3]^{m-/+}$ (R' = H; R-pz^- = $L1a^-$, $L1c^-$, $L1d^-$, $L1g^-$, $L1f^-$; L = Cl^-, NCS^-, py, $CH_3CO_2^-$, $CF_3CO_2^-$ and *m* = 1, 2).[76,88] A shift of the redox potentials has been observed depending on the substituents at the fourth position of the pyrazole ligand and also on the terminal ligand, L.[76,88] The catalytic activity of some trinuclear copper(II) compounds has been tested in the cyclopropanation of styrene[83] and in the peroxidation of alkanes.[84,85]

Mononuclear and trinuclear complexes with pyrazole ligands have been used as starting materials to achieve compounds of higher nuclearity by addition of bridging ligands, such as carboxylate, pyridazine or nitrate ligands.[55,79,92,93] Also, pyrazole-based ligands have been used to bridge mononuclear compounds to form tetranuclear copper(II) compounds,[94] or to bridge two trinuclear units thus forming hexanuclear copper(II) compounds.[80]

Tetranuclear copper(II) compounds can also be synthesized from the copper(II) salt, the pyrazole ligand, another type of ligand and a base. As a result, the pyrazolate anion bridges two dinuclear units.[95,96] An example is the compound with the formula $[Cu_4(L1a)_4L_2]ClO_4$ (HL = 1,3-diamino-2-propanol), in which the dinuclear unit is formed by two copper(II) ions bridged by a pyrazolato ligand and by 1,3-diamino-2-propanol.[95] Another example is the compound $[Cu_4L_2(L1a)_4(CH_3OH)_2](ClO_4)_2$ (L = 1,1-di-(2-pyridyl)-1-methoxymethanol).[96] Magnetic susceptibility studies define both compounds as dinuclear complexes with weak antiferromagnetic interactions between the dinuclear copper(II) units, ascribed to the countercomplementary behaviour of the bridging pyrazole that decreases the value of the magnetic exchange imposed by the other bridging ligand.[95,96] One more example is the compound $[Cu_4F_2(\mu_4\text{-}F)(L1j)_5(HL1j)_4]$ that contains a μ_4-F bridge between the four copper(II) ions that interact antiferromagnetically.[97] A tetranuclear zirconium(IV) compound is obtained by conversion of a dinuclear compound in wet toluene.[98] Tetranuclear heterobimetallic compounds with palladium(II) ions have also been reported.[70,99] Some of the tetranuclear compounds that are reported in the literature were minor side products that were only characterized by X-ray crystallography.[100,101]

Table 1.1. Magnetic and structural data for trinuclear copper(II) compounds.

Compound	Cu–Y–Cu [a]	Cu_3–μ_3-Y [b]	J/cm^{-1} [c]	g [d]	g [e]	Ref
$(PPN)_2[Cu_3(\mu_3\text{-}O)(L1a)_3Cl_3]$	119.59 119.59 120.82	n.r.	−500	2.1	n.r.	74
$(PPN)_2[Cu_3(\mu_3\text{-}OH)(L1a)_3Cl_3]$	118.54 117.26 104.38	0.524	n.r.	n.r.	n.r.	74
$[Cu_3(\mu_3\text{-}OH)(L1a)_3(MeCO_2)_2(HL1a)]$	118.0 115.5 102.6	0.563	< 0	n.r.	$g_{xx} = 2.015$ $g_{yy} = 2.050$ $g_{zz} = 2.200$	83
$[Cu_3(OH)Cl_2(L1a)_3(py)_2]\cdot py$	102.2 113.3 70.93	n.r.	−148 −23	2.17	n.r.	90
$[Cu_3(OH)(L1a)_3(HL1a)_2(NO_3)_2]\cdot H_2O$	112.0 115.0 116.4	0.478	< 0	n.r.	2.1	86
$[Cu_3(\mu_3\text{-}OH)(L1a)_3(HL1a)_2(Me_3CCO_2)_2](Me_3CCOOH)_2$	116.32 111.98 108.40	0.567	−117.7 −90.3 −90.3	2.047	n.r.	89
$(Bu_4N)_2[Cu_3(\mu_3\text{-}Cl)_2(L1a)_3Cl_3]$	86.05	n.r	+28.6	2.07	$g_\perp = 2.05$ $g_\parallel = 2.11$	74, 75
$(Bu_4N)_2[Cu_3(\mu_3\text{-}Br)_2(L1f)_3Br_3]$	77.41-81.07	n.r	+3.1	$g_\perp = 2.46$ $g_\parallel = 2.42$	$g_\perp = 2.01$ $g_\parallel = 2.08$	75
$[Cu_3(\mu_3\text{-}OMe)Cl(L1h)_3(HL1h)_2]Cl$	105.77 105.09 101.87	n.r.	−100	2.19	$g_\perp = 2.21$ $g_\parallel = 1.47$	87
$[Cu_3(\mu_3\text{-}OMe)(L1h)_3Br(HL1h)_2]Br$	107.43 104.61 104.40	n.r.	−103	2.20	$g_\perp = 2.19$ $g_\parallel = 1.59$	87

[a] Cu–Y–Cu angle (Y = O^{2-}, HO^-, Cl^-, Br^-); [b] Distance of μ_3-Y from the Cu_3 plane; [c] The J values describe the magnetic exchange interactions depending on the geometrical parameters of each compound; [d] g-values obtained from the fitting of the magnetic susceptibility data; [e] g-values obtained from EPR measurements; n.r. = not reported; ligand abbreviations HL1a–HL1f are given in Figure 1.4; PPN^+ = bis(triphenylphosphoranylidene)ammonium cation.

The reaction of CuX_2 (X^- = Cl^-, Br^-, NO_3^-) with 3(5)-*tert*-butylpyrazole (HL1i) and sodium methoxide in methanol affords the heptanuclear compounds $[\{Cu_3(HL1i)_6(\mu_3\text{-}X)(\mu_3\text{-}OH)_3\}_2Cu]X_6$ (X^- = Cl^-, Br^-, NO_3^-).[102,103] The use of a ligand with larger steric hindrance at the 3,5-positions of the pyrazole ring precludes the formation of the heptanuclear species and affords a trinuclear compound (as described above).[87] The use of other salts, like CuF_2 yields other products with different nuclearity.[104] The heptanuclear copper(II) compounds are double-cubanes in which a vertex of a copper(II) ion is shared and it is coordinated by six hydroxide ligands. Antiferromagnetic interactions between the copper(II) ions were found in all of the compounds and the magnetic exchange interaction is in the order of correlations made on the Cu–O–Cu angle (so-called Haase correlation)[105] for $[Cu_4(\mu_3\text{-}OR)_4]^{4+}$ and $[Cu_2(\mu\text{-}OH)]^{3+}$ species, leading to a ground state of $S_T = 1/2$.[102,103]

$[Fe_8(\mu_4\text{-}O)_4(L1a)_{12}Cl_4]$ is an octanuclear iron(III) compound which has a Fe_4O_4 cubane structure, where the inner iron(III) ions are connected with the outer iron(III) ions through pyrazole bridges and in which the chloride ligands are at terminal positions.[106] This compound is the first example of an all-iron(III) cubane. Electrochemically four reductions are observed, where the last one is not reversible, but no oxidation process is detected.[106] The compound has an unusual stability due to the $[Fe_4O_4]^{4+}$ core. Replacement of the terminal chloride ligands with other ligands and the introduction of the fourth substituent on the pyrazole ring (HL1b and HL1c) were reported.[107] These compounds exhibit similar redox properties, demonstrating that the $[Fe_4O_4]^{4+}$ core is redox active.[107] Strong antiferromagnetic interactions between the iron(III) ions are present in the compound $[Fe_8(\mu_4\text{-}O)_4(L1a)_{12}Cl_4]$. The fit of the experimental magnetic data indicates strong antiferromagnetic coupling between the inner and the outer iron(III) ions ($J = -50.55$ cm^{-1}), and much weaker coupling is observed between the iron(III) ions within the core ($J = -2.1$ cm^{-1}).[107] The stronger antiferromagnetic interactions between the inner an the outer iron(III) ions are in agreement with the larger Fe–O–Fe angles, *ca.* 119º, as compared with the Fe–O–Fe angles of the inner core, *ca.* 98º. DFT studies were performed to confirm the parameters obtained with the fit of the experimental magnetic susceptibility data.[107] A gallium(III) analogue has also been synthesized.[108] Other examples of octanuclear clusters can be found involving molybdenum(V/VI)[109] or zinc(II) ions.[110] The compound $[Ni(bma)(H_2O)_3][Ni_8(OH)_6(L1a)_{12}]\cdot 6DMSO$ (bma = bis(2-benzinidazolylmethyl)amine) consists of an anionic structure composed from an octanuclear nickel(II) unit, $[Ni_8(OH)_6(L1a)_{12}]^-$ and the cation formed by a mononuclear nickel(II) entity, $[Ni(bma)(H_2O)_3]^+$. In the former case, the eight nickel(II) ions form a cube and the Ni···Ni···Ni angles are around 90º. Antiferromagnetic interactions are present between the nickel(II) ions in the octanuclear anion leading to $S = 0$, but the ground state of the molecule is $S_T = 1$, resulting from the mononuclear counter ion. DFT calculations were performed to estimate the magnetic exchange interactions.[111]

A dodecanuclear copper(II) cage with the formula, $[Cu_{12}(\mu_4\text{-}Cl)_4(\mu_3\text{-}Cl)_2(HL1k)_6(L1k)_4({}^tBuPO_3)_6({}^tBuPO_2OH)_2]$ is formed by combination of phosphonates and pyrazoles as ligands, in which two hexameric units are linked to each other and are stabilized by hydrogen bonding. This compound displays weak antiferromagnetic interactions between the copper(II) ions.[112]

The combination of two pyrazole moieties, *i.e.* bispyrazole ligands, has been used to form tetranuclear copper(II) compounds[113] and also porous coordination polymers with palladium(II), platinum(II), silver(I) or copper(I) ions.[114-117]

1.3.3.3. Pyrazole ligands with substituents containing donor atoms

Substituents with donor atoms on the pyrazole ring can increase the number of possible metal-binding sites that may lead to polynuclear type of compounds. Commonly, the substituents are placed at the 3- and 5-positions of the aromatic ring. Variation of the side arm chain lengths gives some control over metal-metal separation, while the number and type of side arm donor sites allow determining electronic and coordinative properties.[48,118] Recently, a review has been published by Meyer and co-workers, dealing with polynuclear transition metal complexes with compartmental pyrazolate ligands.[23] A main part of this review has been dedicated to dinuclear compounds and therefore they have not been included in this section.

Pyrazole ligands with N-donor substituents, amines

Figure 1.7 shows the ligands used for the compounds described in this section. An important part of this research has been developed by Meyer and co-workers,[119-134] who have studied the coordination ability of the 3,5-bisubstituted pyrazole ligands, with chelating side arms, mainly with N-donor atoms. They mainly differ in the chain lengths of the chelating side arms and the number of donor sites.

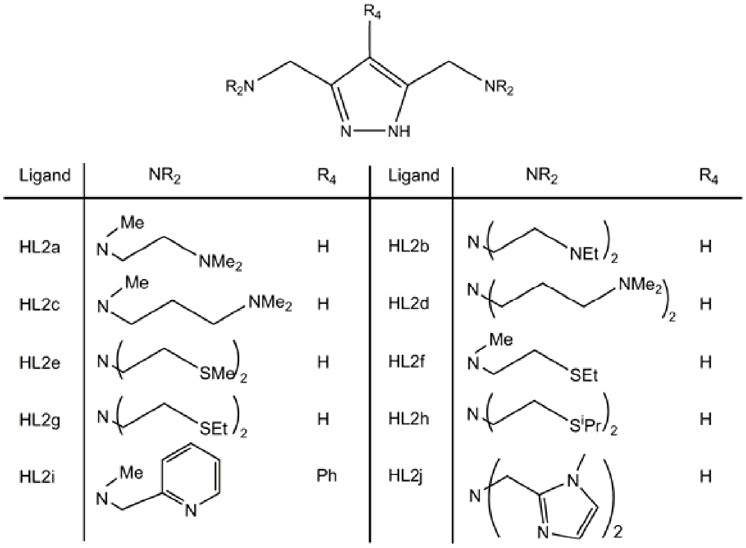


Figure 1.7. Pyrazole-based ligands with N-donor substituents, amines.

Tetranuclear nickel(II) compounds with the general formula $[Ni_4L_2]^{6+}$, have been synthesized with stoichiometric amounts of the metal salt, the pyrazole-based ligand (HL = HL2c–HL2h, see Figure 1.7), the base and the appropriate amount of the bridging ligands, *i.e.* azide and/or carboxylates. The similar central core of these structures is formed by dinuclear nickel(II) units, $[Ni_2L]^{3+}$, that are connected by azide and carboxylate bridges (Figure 1.8).[123-128] Also, the formation of 1-D chains is possible with the assembly of the dinuclear nickel(II) units.[123,131] In Table 1.2 the values of the magnetic exchange interactions for the tetranuclear nickel(II) compounds discussed are shown. In most of the tetranuclear compounds, overall antiferromagnetic interactions are present between the nickel(II) ions (high-spin) leading to a ground state of $S_T = 0$, except for the first four compounds of Table 1.2, in which ferromagnetic interactions between the nickel(II) ions are dominant.[124] Ferromagnetic exchange constants between nickel(II) ions are found in the presence of end-on azido bridges. In the case of end-to-end azido bridges, the $Ni–N_3–Ni$ torsion angle and the Ni–N–N angle are crucial to determine the value of the exchange constant between the nickel(II) ions, as established by common magneto-structural correlations based on the azide bridge.[124-128] Besides exploring azide as bridging ligand, other ligands, such as urea[129] and cyanide[132] have been used in combination with HL2a and HL2b ligands, respectively. With urea as a ligand, a tetranuclear nickel(II) compound is formed, in which the presence of two low-spin nickel(II) ions and two high-spin nickel(II) ions that interact ferromagnetically, is confirmed by magnetic susceptibility studies.[129]

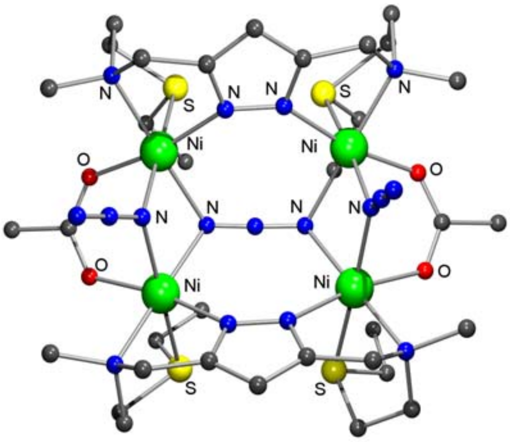


Figure 1.8. Molecular structure of the cation, $[Ni_4(L2f)_2(\mu\text{-}1,1\text{-}N_3)_2(\mu_4\text{-}1,1,3,3\text{-}N_3)(O_2CMe)_2]^+$.[125]

The coordination ability of the HL2a ligand towards other metal ions, such as copper(II) or zinc(II) ions was also explored. The pyrazolato ligand bridges the two metal ions and in some cases, the dinuclear structures, $[M_2L2a]^+$ (M = Cu(II) and Zn(II)), are linked by carbonates taken from the air,[119,122] μ_4-peroxido,[130] phosphato[121] or oxazetidinylacetato.[120] An octanuclear copper(I) compound, that can be described as a $[(MesCu)_4(\mu_4\text{-}O)]^{2-}$ (Mes = 2,4,6-

trimethylphenyl) anion with two dinuclear copper(I)-pyrazole clamps containing the HL2i ligand has also been reported.[134]

Table 1.2. Magnetic data for tetranuclear nickel(II) compounds.

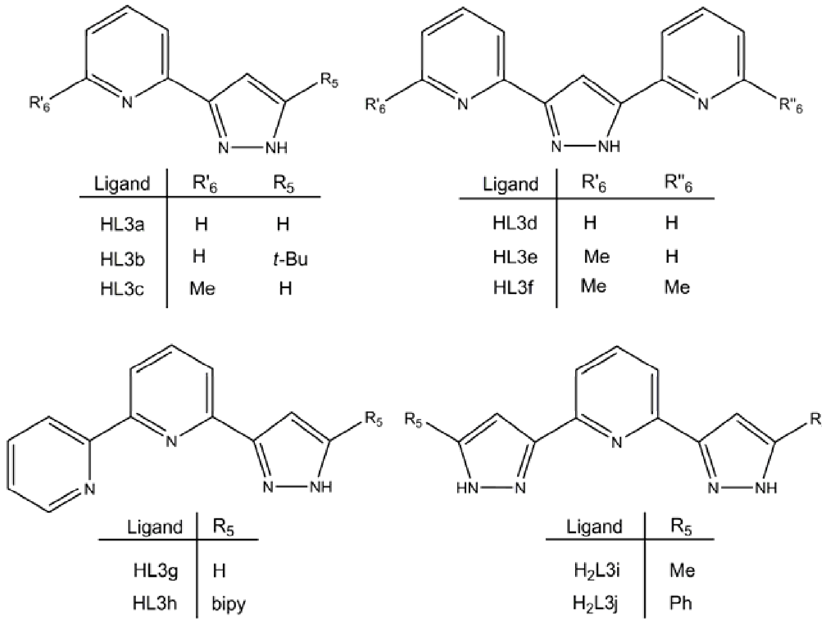
Compound [a]	J / cm^{-1} [b]	g	Ref.
$[Ni_4(L2c)_2(\mu-1,1-N_3)_2(\mu-1,3-N_3)_2](ClO_4)_2\cdot 2CH_4O\cdot 0.5H_2O$	+1.8; +4.2	2.21	124
$[Ni_4(L2c)_2(\mu-1,1-N_3)_2(\mu-1,3-N_3)_2](ClO_4)_2\cdot 2C_3H_6O\cdot C_5H_{12}$	+2.5; +2.5	2.16	124
$[Ni_4(L2c)_2(\mu-1,1-N_3)_2(\mu-1,3-N_3)_2](BPh_4)_2\cdot 2C_3H_6O$	+3.4; −1.0	2.22	124
$[Ni_4(L2d)_2(\mu-1,1-N_3)_2(\mu-1,3-N_3)_2](BPh_4)_2\cdot 2C_3H_6O$	+0.9; −5.8	2.27	124
$[Ni_4(L2d)_2(\mu-1,1-N_3)_2(\mu-1,3-N_3)_2](BPh_4)_2$	+2.0; +4.7	2.19	124
$[Ni_4(L2g)_2(\mu_3-1,1,3-N_3)_2(MeOH)_2](ClO_4)_4$	−42.6; −24.0; +32.1	2.19	123
$[Ni_4(L2f)_2(\mu-1,1-N_3)_2(\mu_4-1,1,3,3-N_3)(O_2CMe)_2]\cdot ClO_4\cdot C_3H_6O$	−110; +106; +2	2.15	125
$[Ni_4(L2f)_2(\mu-1,1-N_3)_2(\mu_4-1,1,3,3-N_3)(O_2CPh)_2]\cdot$ $ClO_4\cdot NaClO_4\cdot 2C_3H_6O\cdot H_2O$	−111; +51; +9	2.15	125
$[Ni_4(L2h)_2(\mu-1,1-N_3)_2(\mu_4-1,1,3,3-N_3)(O_2CMe)_2]\cdot ClO_4$	−133; +129; +26	2.15	125
$[Ni_4(L2h)_2(\mu-1,1-N_3)_2(\mu_4-1,1,3,3-N_3)(O_2CAda)_2]\cdot ClO_4\cdot C_3H_6O$	−111; +86; +5	2.15	125
$[Ni_4(L2e)_2(\mu_4-1,1,3,3-N_3)(O_2CAda)_4]\cdot ClO_4$	−39; +98; −12	2.15	125
$[Ni_4(L2g)_2(\mu_4-1,1,3,3-N_3)(O_2CAda)_4]\cdot ClO_4$	−50; +66; +7	2.15	125
$[Ni_4(L2d)_2(\mu-1,1-N_3)_2(\mu-1,3-N_3)_2](BPh_4)_2\cdot 2C_3H_6O$	−16.2; +2	2.01	126
$[Ni_2(L2c)(\mu-1,1-N_3)(\mu_3-1,1,3-N_3)(N_3)]_2\cdot 2CH_2Cl_2$	−19.7; +6	2.29	126
$[Ni_4(L2g)_2(\mu-1,3-N_3)(\mu_3-1,1,3-N_3)_2(O_2CMe)](ClO_4)_2$	+57; −51; −18; +6	2.29	127
$[Ni_4(L2g)_2(\mu-1,3-N_3)(\mu_3-1,1,3-N_3)_2(O_2CPh)](ClO_4)_2$	+25; −61; −12; +5	2.38	127
$[Ni_4(L2h)_2(\mu-1,3-N_3)(\mu_3-1,1,3-N_3)_2(O_2CPh)](ClO_4)_2$	+27; −53; −3; +6	2.30	127
$[Ni_4(L2g)_2(OCN_2H_4)_2(OCN_2H_3)_2](ClO_4)_2$	+3.4	2.25	129

[a] The azide's nomenclature does not follow the IUPAC's rules. Here μ-1,1-N_3 and μ-1,3-N_3 is used for the end-on and end-to-end bridge, respectively; [b] The J values describe the magnetic exchange interactions depending on the geometrical parameters of each compound. Ligand abbreviations are given in Figure 1.7.

All the compounds reported above contain thioether or amine arms in the amino substituents of the pyrazole ring. The incorporation of other functional groups, such as imidazole (HL2j ligand) has also been studied.[133] In this case, pH potentiometric studies in aqueous solution were performed in combination with the crystallographic characterization of the different polynuclear species formed in the presence of copper(II) ion.[133]

Pyrazole ligands with N-donor substituents, pyridines

2-Pyridylpyrazole derivatives (Figure 1.9) have been proven to be good ligands to obtain different assemblies, such as metallohelicates[135,136] or clusters.[137-145] Together with the employ of another bridging ligand as phosphonate, they provide a good approach to obtain a decanuclear copper(II) cage with the formula $[Cu_5(\mu_3-OH)_2(^tBuPO_3)_3(L3a)_2(MeOH)]_2\cdot 10MeOH\cdot 2H_2O$.[146] The reaction of an iron(II) salt with the 3-(2-pyridyl)-pyrazole ligand formed by the decomposition of the ligand tris[{3-(2-pyridyl)-pyrazol-1-yl}hydroborate] (Tp^{Py}), leads to a tetranuclear compound, $[Fe_4(HL3a)_2(L3a)_6(\mu\text{-}O)_2](PF_6)_2\cdot 4CH_3CN$.[140]



Ligand	R'6	R5
HL3a	H	H
HL3b	H	*t*-Bu
HL3c	Me	H

Ligand	R'6	R"6
HL3d	H	H
HL3e	Me	H
HL3f	Me	Me

Ligand	R5
HL3g	H
HL3h	bipy

Ligand	R5
H_2L3i	Me
H_2L3j	Ph

Figure 1.9. Pyrazole-based ligands with N-donor substituents, pyridines.

The coordination ability of the 3-(2-pyridyl)pyrazole ligand (HL3a) and its derivatives (HL3f, HL3g and HL3h) is also confirmed by the formation of copper(II) tetranuclear grids with the core $[Cu_4L_6]^{2+}$ or $[Cu_4L_4]^{4+}$ (Figure 1.10) in an isolated fashion or in 1-D chains.[138,139,141,143,145] In such a type of grids, strong antiferromagnetic interactions are present between the copper(II) ions. The magnetic behaviour has been explained based on the number of pyrazole bridges and the distorted geometry of the pyrazole ligands.[138,139,141,143,145] Other grid-types of structures are formed with cobalt(II) and manganese(II) ions.[145] However, different typologies and nuclearities can also be found with cobalt(II) ion and HL3f ligand[142] and copper(I) and copper(II) ions with HL3c ligand, respectively.[144]

5-*tert*-Butyl-3-(pyrid-2-yl)-1H-pyrazole (HL3b) is a very versatile ligand, leading to metallocycles (see section 1.3.4). However, in the case of copper(II) salts with non-coordination anions, a cubane-based structure is formed, $[Cu_4(\mu_3\text{-}OH)_4(L3b)_4](ClO_4)_4\cdot x CH_2Cl_2$ (x = 1–2).[147] Small antiferromagnetic interactions between the copper(II) ions are present, as expected by Hatfield and Hodgson's correlation[148] depending on the Cu–O–Cu angle, because the angles found in this compound are within the range where both antiferromagnetic and ferromagnetic interactions can be present. The use of bispyrazole-pyridine ligands (H_2L3i and H_2L3j) affords octanuclear copper(I) compounds.[149]

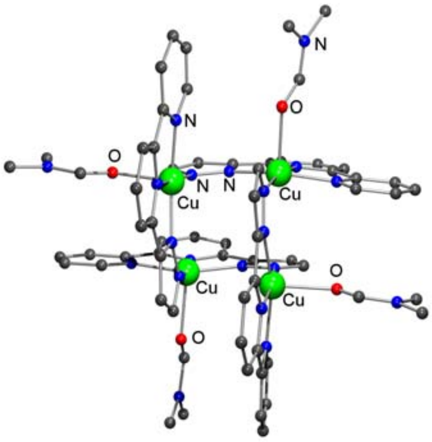
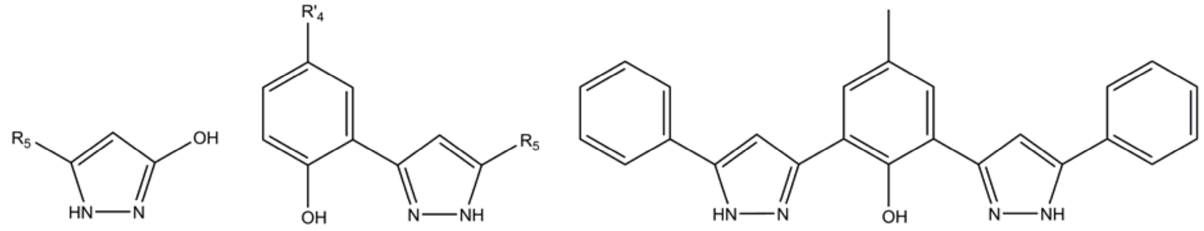


Figure 1.10. Molecular structure of the cation, $[Cu_4(L3g)_4(dmf)_4]^{2+}$.[141]

Pyrazole ligands with O-donor substituents, alcohols

The ligands described in this section, H_2L4a–H_2L4d (Figure 1.11), have been used by Winpenny and co-workers to explore the coordination chemistry of nickel(II) and manganese(II/III) ions. $[Mn_{14}O_2(OH)_4(L4c)_{18}(HL4c)_4(NO_3)_4(H_2O)_4]$ is a mixed-valent compound containing two manganese(III) and twelve manganese(II) ions. Strong antiferromagnetic interactions between the metal centres lead to a ground state of $S_T = 0$.[150] After the synthesis of this cluster and the wheel $[Ni_{24}(OH)_8(L4a)_{16}(O_2CMe)_{24}(HL4a)_{16}]$ that is described below as a metallocycle,[151] derivatives of pyrazolinol-type of ligands (HL4b, HL4c, HL4d) were synthesized to study the reactivity towards nickel(II) ions in the presence of pivalate (piv^-) bridging ligands. As a result, different topologies have been obtained with nuclearities ranging from $[Ni_4Na_4]$, $[Ni_5Na_4]$, $[Ni_5Li_6]$, $[Ni_8M_2]$ (M = K(I), Rb(I), Cs(I)) and $[Ni_8]$.[152] Antiferromagnetic interactions between the nickel(II) ions are present leading to a zero spin or low-spin ground state in most of the cases, except for $[Ni_5Li_6]$ and $[Ni_8]$ in which ferromagnetic interactions are operative, yielding a ground state of $S_T \geq 1$ and $S_T = 6$, respectively.[152] $[Ni_8M_2]$ and $[Ni_8]$ clusters are formed by two pseudo-cubanes linked by μ-O bridges.[152] The differences in the magnetic behaviour of both types of clusters are explained in terms of the magneto-structural correlations within the $[Ni_4(\mu_3\text{-}O)_4]$ core, in which Ni–O–Ni angles smaller than 99º favour ferromagnetic interactions, whereas larger angles promote antiferromagnetic interactions.[152] The incorporation of alkaline metals in the final structure of some of the compounds led to an extension of the study with alkaline-earth metal ions.[153] In this case, the reactions were also performed with the dinuclear complex $[Ni_2(H_2O)(piv)_4(Hpiv)_4]$ as a starting material and with HL4c, forming $[Ni_6Mg_2(OH)_2(L4c)_4(piv)_{10}(HL4c)_4(MeOH)_2]$ and $[Ni_8M]$ (M = Sr(II), Ba(II)) clusters.[153] The first compound is formed by two nickel(II) triangles bridged by magnesium(II) ions. Ferromagnetic exchange interactions are present between the nickel(II) ions forming the triangle. The nonanuclear compounds, $[Ni_8Sr(OH)_2(L4c)_6(piv)_{10}(HL4c)_5(Hpiv)_2(CH_3CN)]$ and $[Ni_8Ba(OH)_2(L4c)_6(piv)_{10}(HL4c)_{5.3}(Hpiv)_{0.7}(CH_3CN)_2]$ are formed by two tetranuclear nickel(II) units bridged by strontium(II) and barium(II) ions, respectively. Dominant antiferromagnetic interactions are present between the nickel(II) ions leading to two independent ground states both with $S_T = 2$ corresponding to the two tetranuclear units. The use of silver(I) as a second metal ion resulted in the serendipitous formation of the large antiferromagnetic cluster $[Ni_{21}Ag(\mu_4\text{-}OH)_4(\mu_3\text{-}OH)_6(L4d)_{13}(piv)_{20}(Hpiv)_4(CH_3CN)_{3.5}(H_2O)_{0.5}]$.[154] The exploration of new carboxylic acids, *i.e* *t*-butylbenzoic acid and benzoic acid, and the introduction of azido ligands have demonstrated the unpredictability of the pyrazolinone ligands with three new compounds, $Na[Ni_8Na(OH)_2F_8({}^tBuPhCO_2)_8(HL4a)_8]$, $[Ni_8Na_2(N_3)_{12}({}^tBuPhCO_2)_2(L4a)_4(HL4a)_6(EtOAc)_6]$ and $[Ni_8Na_2(N_3)_{12}(PhCO_2)_2(L4a)_4(HL4a)_6(EtOAc)_6]$.[155] Figure 1.12 shows the molecular structure of $[Ni_8Na_2(N_3)_{12}(PhCO_2)_2(L4a)_4(HL4a)_6(EtOAc)_6]$, in which ferromagnetic interactions between the nickel(II) ions are propagated through the azide groups; micro-Squid measurements indicate a single-molecule magnet behaviour.[155]



Ligand	R_5
H_2L4a	Me
H_2L4b	Et
H_2L4c	Ph
H_2L4d	CF_3

Ligand	R'_4	R_5
H_2L5a	H	H
H_2L5b	Me	H
H_2L5c	Br	H
H_2L5d	H	Me

H_3L5e

Figure 1.11. Pyrazole-based ligands with O-donor substituents, alcohols and phenols (H_2L5a and H_2L5d are called H_2phpzH and $H_2phpzMe$, respectively, in the following chapters).

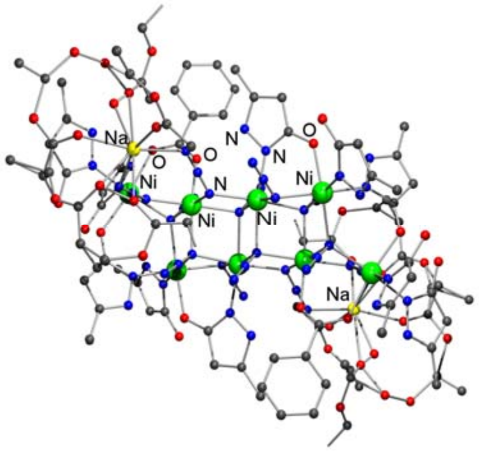


Figure 1.12. Molecular structure of $[Ni_8Na_2(N_3)_{12}(PhCO_2)_2(L4a)_4(HL4a)_6(EtOAc)_6]$.[155]

Pyrazole ligands with O-donor substituents, phenols

The phenol-pyrazole based ligands used for the compounds described in this section are shown in Figure 1.11. An octanuclear manganese(III) compound with the formula $[Mn_8(\mu_4\text{-}O)_4(L5d)_8(thf)_4]$ has been reported by Reedijk and co-workers, in which strong antiferromagnetic interactions are operative between all the manganese(III) ions (Figure 1.13).[30] This compound resembles other octanuclear iron(III) compounds with a cubane core, described above.[106,107] A tetranuclear nickel(II) compound with the formula $[Ni_4(OH)(OMe)_3(HL5d)_4(MeOH)_3]\cdot MeOH$ has also been reported with the same ligand, H_2L5d (also called $H_2phpzMe$).[26] Ferromagnetic interactions are present leading to a ground state of $S_T = 4$. Trinuclear oxide-centred compounds are obtained with similar phenol-pyrazole ligands, $[Mn_3(\mu_3\text{-}O)(L)_3(O_2CMe)(MeOH)_x]$ ($H_2L = H_2L5a$, H_2L5b and $x = 3, 4$) which form 1-D chains due to the acetate ligands that bridge the different trinuclear units.[31] Long-range magnetic ordering was found in one of these compounds. If the methanol is replaced by ethanol, $[Mn_3(\mu_3\text{-}O)(L5b)_3(O_2CMe)(EtOH)_4]$ is formed. In this case, the chains are more isolated and the compound behaves as single-chain magnet below 4 K.[27] The influence of the solvent on the magnetic properties has also been observed in similar trinuclear manganese(III) units containing the ligand H_2L5c.[156,157] Tao and co-workers extended the chemistry of these types of ligands with other transition-metal ions, such as the copper(II) ion.[28] The result is the formation of large cages with the formula $(HNEt_3)_2[Cu_{21}(CH_3CN)_2(H_2O)(\mu\text{-}N_3)_6(\mu_3\text{-}N_3)_2(L5a)_{18}]\cdot 3H_2O\cdot 2EtOH$ and $[Cu_{16}(EtOH)_2(H_2O)_2(L5b)_{16}]\cdot 9.5H_2O$.[28] Predominant antiferromagnetic interactions were found between the copper(II) ions in both compounds, although some ferromagnetic interactions are present between some of the copper(II) ions in $(HNEt_3)_2[Cu_{21}(CH_3CN)_2(H_2O)(\mu\text{-}N_3)_6(\mu_3\text{-}N_3)_2(L5a)_{18}]\cdot 3H_2O\cdot 2EtOH$. Monte Carlo simulations were performed to evaluate the magnitude of the magnetic exchange interactions.[28] A phenol-bis(pyrazole) ligand was used to synthesize a mixed-valence manganese(II/III) linear trinuclear compound, $[Mn_3(HL5e)_2(O_2CMe)_3(MeOH)_3]$.[29] Antiferromagnetic interactions between the manganese(II/III) ions are present in the molecule, leading to a ground state of $S_T = 3$.[29]

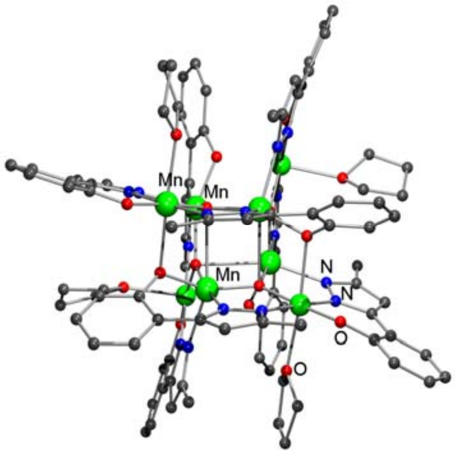


Figure 1.13. Molecular structure of $[Mn_8(\mu_4\text{-}O)_4(L5d)_8(thf)_8]$.[30]

Pyrazole ligands with other functional groups with N- and/or O-donor substituents

In this section, compounds with ligands that cannot be described under the previous classifications are presented (Figure 1.14).

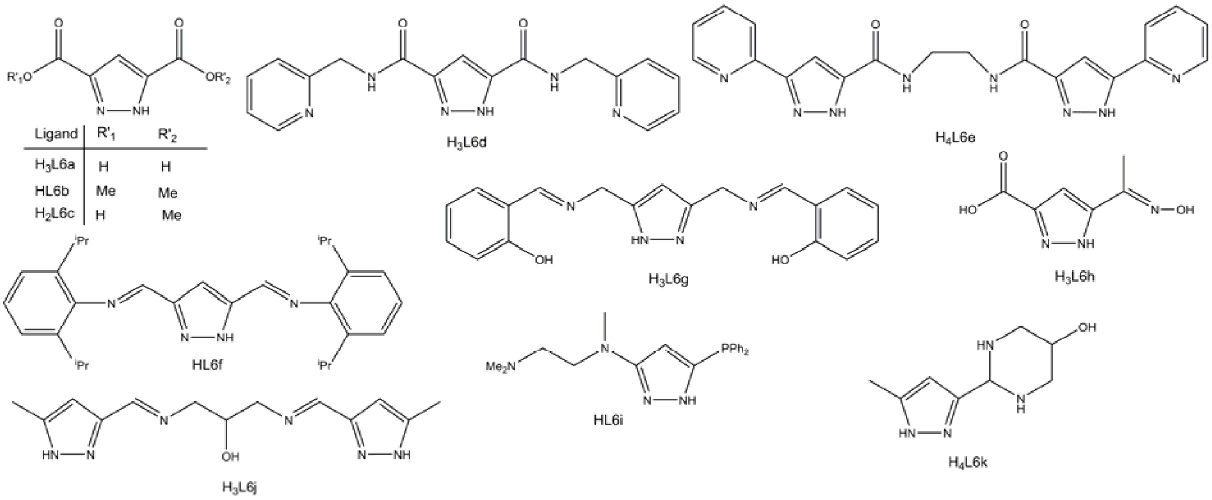


Figure 1.14. Pyrazole-based ligands with other functional groups with N- and/or O-donor substituents.

The functionalization of the pyrazole ligand with acid groups as substituents on the pyrazole ring, *i.e.* 3,5-pyrazoledicarboxylic acid (H_3L6a), introduces numerous coordination sites. Coordination polymers have been obtained by hydrothermal synthesis with a variety of transition metal ions[158-160] and a combination of 3d and 4f metals ions, such as $Cu^{II}Ln^{III}_2$.[161] An example with the 3,5-pyrazoledicarboxylic acid as a ligand, is a trinuclear copper(II) compound with formula $[Cu_3(L6a)_2(H_2O)_4]_n$.[158] Strong antiferromagnetic interactions between the copper(II) ions are mediated by the pyrazole ligand, and weaker ferromagnetic and antiferromagnetic interactions between the copper(II) ions are mediated by the carboxylate ligands in *syn-anti*-equatorial-equatorial and *syn-anti*-axial-equatorial type of bridge, respectively.[158] Decomposition of an amide-pyrazole derivative ligand to $L6a^{3-}$ ligand during the synthesis, resulted in the formation of trinuclear linear copper(II) compounds.[162] Magnetic susceptibility studies revealed weak antiferromagnetic interactions, ascribed to the large separation between the copper(II) ions.[162] The HL6b ligand has been used in the synthesis of a linear trinuclear copper(II) compound.[163] Hydrolysis of the HL6b ligand during the synthesis resulted in the formation of a tetranuclear copper(II) compound containing the HL6c ligand. Weak antiferromagnetic interactions between the copper(II) ions are observed.[164]

Pyrazole-3,5-dicarboxamides are often used as intermediates in the synthesis of pyrazoles with chelating amine side arms. Therefore the coordination ability of this type of ligands has also been studied, because when the amide is deprotonated, the metal ion can coordinate through the N-atoms, whereas if it remains protonated the coordination would be through the oxygen. The ligand *N,N'*-bis(2-pyridylmethyl)pyrazole-3,5-dicarboxamide (H_3L6d) forms tetranuclear [2×2] grids with the general formula $[M_4(HL6d)_4]\cdot 8H_2O$ (M = Cu(II), Ni(II)).[165] Magnetic susceptibility and EPR studies were performed only for the copper(II) compound.[165] The nickel(II) compound is diamagnetic, whilst antiferromagnetic interactions between the copper(II) ions are mediated by the pyrazole bridges. Other examples of tetranuclear nickel(II) and copper(II) compounds have been reported with amide-pyrazole ligands, *i.e.* with the H_4L6e ligand.[166,167] These compounds have different topology depending on the metal ion, linear for nickel(II) ions and helical for copper(II) ions.[167] Weak and strong antiferromagnetic interactions have been found, respectively, between the metal ions.[167] Heterobimetallic compounds are also reported with the same ligand.[166]

Diimine-pyrazole ligands are known to stabilize large clusters.[168-170] Two hexanuclear nickel(II) compounds have been reported composed of three bimetallic units, $[Ni_2(L6f)X_3]$ (X^- = Cl^-, Br^-) bridged by the halogen (Figure 1.15).[168,169] Also, hexanuclear copper(II) compounds are obtained with the same ligand.[170] EPR and magnetic susceptibility studies revealed strong antiferromagnetic interactions between the copper(II) ions. A linear tetranuclear manganese(III) compound has been reported with H_3L6g, in which the salicylideneaminate moiety acts as chelating ligand and the pyrazole ligand bridges the manganese(III) ions.[171] Weak antiferromagnetic interactions between the manganese(III) ions are observed.[171]

The coordination ability of ligands containing two different donor groups in the substituents of the pyrazole ligand has also been explored.[172,173] As a result, a linear trinuclear copper(II) compound has been synthesized with the H_3L6h ligand that contains both an oxime and an acid substituent group. Strong antiferromagnetic interactions between the copper(II) ions are operative in this compound.[173] Another example is a tetranuclear nickel(II) compound with the HL6i ligand in which the nickel(II) ions are in low-spin electronic configuration.[172] A linear tetranuclear copper(II) compound was synthesized containing two different types of pyrazolate ligands, H_3L6j and H_3L6k.[174] Strong antiferromagnetic interaction between the copper(II) ions is present, as concluded from magnetic susceptibility and EPR studies.[174]

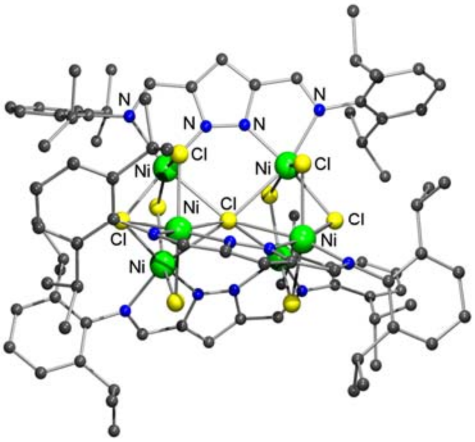


Figure 1.15. Molecular structure of $[Ni_2(L6f)Cl_3]$.[168,169]

1.3.4. Metallocycles

Metal-directed self-assembly processes often form well-defined architectures.[175-178] Cyclic metal-organic compounds with a central cavity or metallocycles are one of these structural examples found in supramolecular chemistry.[175-178] Some examples with pyrazole-based ligand have been reported in the literature.[55,97,104,179-182] An octanuclear copper(II) wheel, $[Cu_8(L1k)_8(OH)_8]$ (HL1k = 3,5-dimethylpyrazole), was formed by oxidation of $[Cu(L1k)]_n$, which is catalytically active in some oxidation reactions.[55] The reaction of the wheel with primary alcohols affords the octaalkoxido derivatives.[55] The removal of the chloride anion from $[(Cu_3(\mu_3\text{-}O)(L1a)_3Cl_3]^{2-}$ and $[(Cu_3(\mu_3\text{-}Cl)_2(L1a)_3Cl_3]^{2-}$ affords the rings $[\{cis\text{-}Cu(\mu\text{-}OH)(L1a)\}_n]$ (n = 6, 8, 9, 12 and 14), where the distorted square-planar copper(II) ions are connected by μ-pz ligands at the outside of the ring and μ-OH ligands at the inner side of the ring.[180] Two of these units encapsulate different ions (chloride, carbonate and sulfate) that are stabilized by the numerous weak hydrogen bonds. The ring size is not dependent of the encapsulated anion.[180] Copper(II) cages of smaller nuclearity have also been reported.[97,179] An example is the compound $[\{Cu_3(HL1i)_4(L1i)_2(\mu\text{-}F)_2(\mu_3\text{-}F)\}_2]F_2$ (HL1i = 5-*tert*-butylpyrazole) in which antiferromagnetic interactions are present between the copper(II) ions, the stronger path being the one mediated by the $[Cu(\mu\text{-}F)_2]^{2+}$ bridges.[104] Another example is the hexanuclear copper(II) cage $[Au(PPh_3)_2][Cu_6(\mu\text{-}OH)_6(L1l)_6Cl]$ (HL1l = 3,5-di(trifluoromethyl)-pyrazole), in which strong antiferromagnetic interactions are present between the copper(II) ions.[181] The zinc(II) ion has also been found suitable for the formation of a neutral macrocycle,[182] in which the mercaptoethanol ligands are inside the ring and the pyrazole ligands are at the outside; a channel with a diameter of 4.7 Å is generated from this structure.

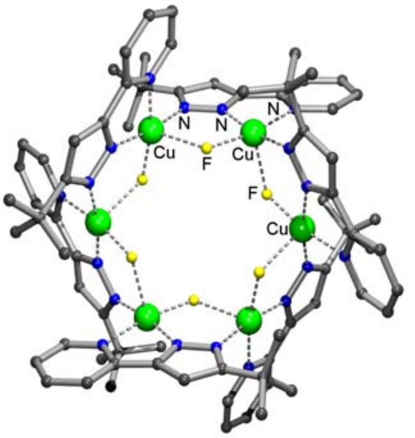


Figure 1.16. Molecular structure of the metallocycle [{Cu(μ-F)(μ-(L3b)}$_6$].[183]

Pyrazole ligands bearing substituents with donor atoms are also capable of forming metallocycles.[97,151,183-185] The 3(5)-pyrid-2-yl)-5-(3)-(*tert*-butyl)pyrazole ligand (HL3b) affords a metallocrown with the formula [{Cu(μ-F)(μ-(L3b)}$_6$(H$_2$O)$_2$]·8CH$_2$Cl$_2$ (Figure 1.17).[184] The study of guest molecules, such as Na$^+$, K$^+$, NH$_4^+$, MeNH$_3^+$ and four amino acids has been carried out.[183] Larger guests cannot bind inside the cavity; therefore they bind exogenously to the two bowl-shaped cavities.[183] Strong hydrogen bonds stabilize all the structures.[183,184] Magnetic susceptibility studies reveal antiferromagnetic interactions that are barely affected by the guest binding.[183] The use of less-coordinating anions of the copper(II) salt affords tetranuclear compounds.[97] Other metal ions such as cobalt(II) afford the mixed-valence Co(II/III) metallocrown, [Co$_6$(μ-OH)$_6$(μ-(L3b)$_6$]$^{m+}$ (m = 2 or 3).[185] A large cage is formed by 24 high-spin nickel(II) ions in [Ni$_{24}$(OH)$_8$(L4a)$_{16}$(O$_2$CMe)$_{24}$(HL4a)$_{16}$] (HL4a = 3-methyl-3-pyrazolin-5-one).[151] It is described as an octamer of chemically trinuclear-based building blocks. Antiferromagnetic interactions between the nickel(II) ions are present and even at low temperature many excited states are populated.[151]

1.3.5. Metallohelicates

Another group of supramolecular architectures is formed by metallohelicates, based on not only coordinative bonds, but also on intermolecular noncovalent interactions, such as electrostatic interactions, hydrogen bonding and π–π stacking.[186,187] Only a few examples have been reported so far involving pyrazole ligands.[135,136] Actually, all of them contain the same ligand, 3,5-bis(2-pyridyl)pyrazole (HL3d). The compounds [{M(μ-L3d)$_3$}$_2${M(μ-OH)}](SCN)$_3$·6H$_2$O (M = Ni(II), Zn(II)) were synthesized using solvothermal conditions.[135]

In such compounds, the $[Ni_3(\mu\text{-}OH)]^{5+}$ cluster core is wrapped by two terminal $[Ni(\mu\text{-}L3d)_3]^-$ units with SCN^- as a counter anion.[135] These compounds were used in combination with CuSCN to obtain other compounds, $[Cu_{12}(CN)_{11}(SCN)_4][\{M(\mu\text{-}L3d)_3\}_2\{M(\mu\text{-}OH)\}]$ (M = Ni(II), Zn(II)),[135] in which the double-helical strands are stabilized by the hydrogen bonding. Antiferrromagnetic interactions between the nickel(II) ions were found in $[\{Ni(\mu\text{-}L3d)_3\}_2\{Ni(\mu\text{-}OH)\}](SCN)_3{\cdot}6H_2O$ and $[Cu_{12}(CN)_{11}(SCN)_4][\{Ni(\mu\text{-}L3d)_3\}_2\{Ni(\mu\text{-}OH)\}]$.[135] Another example is the compound $[\{Fe(\mu\text{-}L3d)_3\}_2Fe_3(\mu\text{-}O)](NCS)_2{\cdot}10H_2O$ (Figure 1.17), where the core $[Fe_3O]^{4+}$ with high-spin iron(II) ions is wrapped by two $[Fe(L3d)_3]^-$ units with low-spin iron(II) ions.[136] Mössbauer spectroscopy confirmed the oxidation states of the iron(II) ions and antiferromagnetic interactions between high-spin iron(II) ions were found to be present in the core.[136]

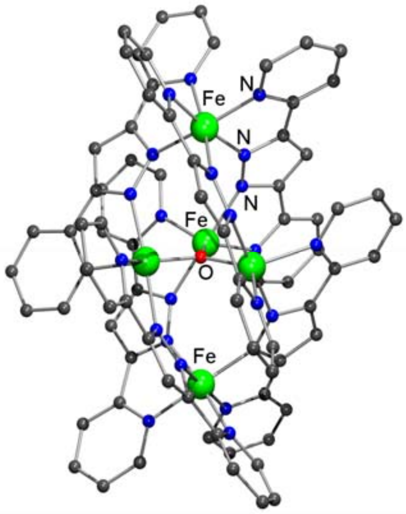


Figure 1.17. Molecular structure of $[\{Fe(\mu\text{-}L3d)_3\}_2Fe_3(\mu\text{-}O)](NCS)_2{\cdot}10H_2O$.[136]

To conclude, pyrazole-based ligands are very versatile ligands, since they are able to form different architectures, from polynuclear clusters to metallocycles or metallohelicates. The incorporation of other coordinating groups to the pyrazole ring increases the variety of polymetallic compounds that can be formed. In addition to the ability to bridge two or more metal ions, pyrazole ligands also provide an effective magnetic exchange pathway between them,

1.4. References

1. Rubahn, H.-G., *Basics on Nanotechnology*. Wiley VCH: Weinheim, 2008.
2. Martin, J. I.; Nogues, J.; Liu, K.; Vicent, J. L.; Schuller, I. K., *J. Magn. Magn. Mater.,* **2003**, 256, 449-501.
3. Gatteschi, D.; Sessoli, R.; Villain, J., *Molecular Nanomagnets*. Oxford University Press: Oxford, 2006.
4. Teo, B. K.; Sun, X. H., *J. Clust. Sci.,* **2006**, 17, 529-540.
5. *Molecular Magnetism: From Molecular Assemblies to the Devices*. Coronado, E.; Delhaès, P.; Gatteschi, D.; Miller, J. S., Eds. Kluwer Academic Publishers: Dordrecht, 1996.
6. *Magnetism: A Supramolecular Function*. Kahn, O., Ed. Kluwer Academic Publishers: Dordrecht, 1996.
7. Kahn, O., *Molecular Magnetism*. Wiley-VCH: New York, 1993.
8. Winpenny, R. E. P., *J. Chem. Soc.-Dalton Trans.,* **2002**, 1-10.
9. Aromí, G.; Aubin, S. M. J.; Bolcar, M. A.; Christou, G.; Eppley, H. J.; Folting, K.; Hendrickson, D. N.; Huffman, J. C.; Squire, R. C.; Tsai, H. L.; Wang, S.; Wemple, M. W., *Polyhedron,* **1998**, 17, 3005-3020.
10. Winpenny, R. E. P., *Adv. Inorg. Chem.,* **2001**, 52, 1-111.
11. Lescouëzec, R.; Toma, L. M.; Vaissermann, J.; Verdaguer, M.; Delgado, F. S.; Ruiz-Pérez, C.; Lloret, F.; Julve, M., *Coord. Chem. Rev.,* **2005**, 249, 2691-2729.
12. Thompson, L. K.; Waldmann, O.; Xu, Z. Q., *Coord. Chem. Rev.,* **2005**, 249, 2677-2690.
13. Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusukawa, T.; Biradha, K., *Chem. Commun.,* **2001**, 509-518.
14. Saalfrank, R. W.; Bernt, I.; Chowdhry, M. M.; Hampel, F.; Vaughan, G. B. M., *Chem.-Eur. J.,* **2001**, 7, 2765-2769.
15. Berlinguette, C. P.; Vaughn, D.; Cañada-Vilalta, C.; Galán-Mascarós, J. R.; Dunbar, K. R., *Angew. Chem.-Int. Edit.,* **2003**, 42, 1523-1526.
16. Marvaud, V.; Decroix, C.; Scuiller, A.; Guyard-Duhayon, C.; Vaissermann, J.; Gonnet, F.; Verdaguer, M., *Chem.-Eur. J.,* **2003**, 9, 1677-1691.
17. Marvaud, V.; Decroix, C.; Scuiller, A.; Tuyeras, F.; Guyard-Duhayon, C.; Vaissermann, J.; Marrot, M.; Gonnet, F.; Verdaguer, M., *Chem.-Eur. J.,* **2003**, 9, 1692-1705.
18. Miyasaka, H.; Saitoh, A.; Abe, S., *Coord. Chem. Rev.,* **2007**, 251, 2622-2664.
19. Ajò, D.; Bencini, A.; Mani, F., *Inorg. Chem.,* **1988**, 27, 2437-2444.
20. Matsushima, P.; Hamada, H.; Watanabe, K.; Koikawa, M.; Tokii, T., *J. Chem. Soc.-Dalton Trans.,* **1999**, 971-977.
21. Nishida, Y.; Kida, S., *Inorg. Chem.,* **1988**, 27, 447-452.
22. Tanase, S.; Koval, I. A.; Bouwman, E.; de Gelder, R.; Reedijk, J., *Inorg. Chem.,* **2005**, 44, 7860-7861.
23. Klingele, J.; Dechert, S.; Meyer, F., *Coord. Chem.Rev.,* **2009**, doi:10.16/j.ccr.2009.03.026.
24. LaMonica, G.; Ardizzoia, G. A., *Progr. Inorg. Chem.,* **1997**, 46, 151-238.
25. Halcrow, M. A., *Dalton Trans.,* **2009**, 2059-2073.
26. Aromí, G.; Bouwman, E.; Burzuri, E.; Carbonera, C.; Krzystek, J.; Luis, F.; Schlegel, C.; van Slageren, J.; Tanase, S.; Teat, S. J., *Chem.-Eur. J.,* **2008**, 14, 11158-11166.
27. Bai, Y. L.; Tao, J.; Wernsdorfer, W.; Sato, O.; Huang, R. B.; Zheng, L. S., *J. Am. Chem. Soc.,* **2006**, 128, 16428-16429.
28. Bai, Y. L.; V., T.; Huang, R. B.; Zheng, L. S.; Tao, J., *Chem.-Eur. J.,* **2009**, 15, 2377-2383.
29. Barrios, L. A.; Aromí, G.; Ribas, J.; Uber, J. S.; Roubeau, O.; Sakai, K.; Masaoka, S.; Gamez, P.; Reedijk, J., *Eur. J. Inorg. Chem.,* **2008**, 3871-3876.
30. Tanase, S.; Aromí, G.; Bouwman, E.; Kooijman, H.; Spek, A. L.; Reedijk, J., *Chem. Commun.,* **2005**, 3147-3149.
31. Tao, J.; Zhang, Y. Z.; Bai, Y. L.; Sato, O., *Inorg. Chem.,* **2006**, 45, 4877-4879.
32. Tanase, S.; Bouwman, E.; Long, G. J.; Shahin, A. M.; Mills, A. M.; Spek, A. L.; Reedijk, J., *Eur. J. Inorg. Chem.,* **2004**, 4572-4578.
33. Greenwood, N. N.; Earnshaw, A., *Chemistry of the elements*. Pergamon Press: London, 1984.

34. Carlin, R. L., *Magnetochemistry*. Springer Verlag: Berlin, 1986.
35. Viciano-Chumillas, M.; Marqués-Giménez, M.; Tanase, S.; Evangelisti, M.; Mutikainen, I.; Turpeinen, M.; Smits, J. M. M.; de Gelder, R.; de Jongh, L. J.; Reedijk, J., *J. Phys. Chem. C,* **2008**, 112, 20525–20534.
36. Viciano-Chumillas, M.; Tanase, S.; Mutikainen, I.; Turpeinen, M.; de Jongh, L. J.; Reedijk, J., *Inorg.Chem.,* **2008**, 47, 5919-5929.
37. Viciano-Chumillas, M.; Tanase, S.; Mutikainen, I.; Turpeinen, U.; de Jongh, L. J.; Reedijk, J., *Dalton Trans.,* **2009**, 7445-7453.
38. Viciano-Chumillas, M.; Tanase, S.; Aromí, G.; Smits, J. M. M.; de Gelder, R.; Solans, X.; Bouwman, E.; Reedijk, J., *Eur. J. Inorg. Chem.,* **2007**, 2635-2640.
39. Constable, E. C.; Steel, P. J., *Coord. Chem. Rev.,* **1989**, 93, 205-223.
40. Reedijk, J., in *Comprehensive Coordination Chemistry*, Wilkinson, G., Gillard, R.D., Mc Cleverty, J.A., Ed. Pergamon: Oxford, 1987; Vol. II, pp 73-98.
41. Fusco, R., in *Chemistry of Heterocyclic Compounds: A Series of Monographs*, Wiley, R. H. B., L. C.; Fusco, R., Jarboe, C.H., Ed. John Wiley & Sons, Ltd.: New York, 1967; Vol. 22, pp 1-174.
42. Büchner, E., *Chem. Ber.,* **1889**, 22, 842-847.
43. Trofimenko, S., *Chem. Rev.,* **1972**, 72, 497-509.
44. Trofimenko, S., *Adv. Chem.,* **1976**, 289-301.
45. Trofimenko, S., *Progr. Inorg. Chem.,* **1986**, 34, 115-210.
46. Trofimenko, S., *Chem. Rev.,* **1993**, 93, 943-980.
47. Halcrow, M. A., *Coord. Chem. Rev.,* **2005**, 249, 2880-2908.
48. Mukherjee, R., *Coord. Chem. Rev.,* **2000**, 203, 151-218.
49. Reedijk, J., *Recl. Trav. Chim. Pays-Bas,* **1970**, 89, 605-619.
50. Sadimenko, A. P.; Basson, S. S., *Coord. Chem. Rev.,* **1996**, 147, 247-297.
51. Maekawa, M.; Munakata, M.; Kuroda, T.; Nozaka, Y., *Inorg. Chim. Acta,* **1993**, 208, 243-244.
52. Rettig, S. J.; Storr, A.; Summers, D. A.; Thompson, R. C.; Trotter, J., *Can. J. Chem.-Rev. Can. Chim.,* **1997**, 75, 949-958.
53. Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J., *Can. J. Chem.-Rev. Can. Chim.,* **1993**, 71, 1425-1436.
54. Miras, H. N.; Zhao, H.; Herchel, R.; Rinaldi, C.; Perez, S.; Raptis, R. G., *Eur. J. Inorg. Chem.,* **2008**, 4745-4755.
55. Ardizzoia, G. A.; Angaroni, M. A.; La Monica, G.; Cariati, F.; Cenini, S.; Moret, M.; Masciocchi, N., *Inorg. Chem.,* **1991**, 30, 4347-4353.
56. Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J., *Can. J. Chem.-Rev. Can. Chim.,* **1992**, 70, 2161-2173.
57. Ehlert, M. K.; Storr, A.; Thompson, R. C., *Can. J. Chem.-Rev. Can. Chim.,* **1992**, 70, 1121-1128.
58. Masciocchi, N.; Galli, S.; Alberti, E.; Sironi, A.; Di Nicola, C.; Pettinari, C.; Pandolfo, L., *Inorg. Chem.,* **2006**, 45, 9064-9074.
59. Morawitz, T.; Lerner, H. W.; Bolte, M., *Acta Cryst. E,* **2006**, 62, M1474-M1476.
60. Murray, H. H.; Raptis, R. G.; Fackler, J. P., *Inorg. Chem.,* **1988**, 27, 26-33.
61. Omary, M. A.; Rawashdeh-Omary, M. A.; Gonser, M. W. A.; Elbjeirami, O.; Grimes, T.; Cundari, T. R., *Inorg. Chem.,* **2005**, 44, 8200-8210.
62. Raptis, R. G.; Fackler, J. P., *Inorg. Chem.,* **1988**, 27, 4179-4182.
63. Dias, H. V. R.; Diyabalanage, H. V. K., *Polyhedron,* **2006**, 25, 1655-1661.
64. Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J., *Can. J. Chem.-Rev. Can. Chim.,* **1990**, 68, 1444-1449.
65. Masciocchi, N.; Moret, M.; Cairati, P.; Sironi, A.; Ardizzoia, G. A.; La Monica, G., *J. Am. Chem. Soc.,* **1994**, 116, 7668-7676.
66. Mohamed, A. A.; Pérez, L. M.; Fackler, J. P., *Inorg. Chim. Acta,* **2005**, 358, 1657-1662.
67. Dias, H. V. R.; Diyabalanage, H. V. K.; Eldabaja, M. G.; Elbjeirami, O.; Rawashdeh-Omary, M. A.; Omary, M. A., *J. Am. Chem. Soc.,* **2005**, 127, 7489-7501.
68. Mohamed, A. A.; Burini, A.; Fackler, J. P., *J. Am. Chem. Soc.,* **2005**, 127, 5012-5013.

69. Mohamed, A. A.; Galassi, R.; Papa, F.; Burini, A.; Fackler, J. P., *Inorg. Chem.,* **2006**, 45, 7770-7776.
70. Umakoshi, K.; Yamauchi, Y.; Nakamiya, K.; Kojima, T.; Yamasaki, M.; Kawano, H.; Onishi, M., *Inorg. Chem.,* **2003**, 42, 3907-3916.
71. Umakoshi, K.; Kojima, T.; Kim, Y. H.; Onishi, M.; Nakao, Y.; Sakaki, S., *Chem.-Eur. J.,* **2006**, 12, 6521-6527.
72. Piñero, D.; Baran, P.; Boča, R.; Herchel, R.; Klein, M.; Raptis, R. G.; Renz, F.; Sanakis, Y., *Inorg. Chem.,* **2007**, 46, 10981-10989.
73. Lukasiewicz, M.; Ciunik, Z.; Mazurek, J.; Sobczak, J.; Staron, A.; Wolowiec, S.; Ziolkowski, J. J., *Eur. J. Inorg. Chem.,* **2001**, 1575-1579.
74. Angaridis, P. A.; Baran, P.; Boča, R.; Cervantes-Lee, F.; Haase, W.; Mezei, G.; Raptis, R. G.; Werner, R., *Inorg. Chem.,* **2002**, 41, 2219-2228.
75. Boča, R.; Dlhan, L.; Mezei, G.; Ortiz-Perez, T.; Raptis, R. G.; Telser, J., *Inorg. Chem.,* **2003**, 42, 5801-5803.
76. Mezei, G.; McGrady, J. E.; Raptis, R. G., *Inorg. Chem.,* **2005**, 44, 7271-7273.
77. Mezei, G.; Raptis, R. G., *Inorg. Chim. Acta,* **2004**, 357, 3279-3288.
78. Mezei, G.; Raptis, R. G.; Telser, J., *Inorg. Chem.,* **2006**, 45, 8841-8843.
79. Mezei, G.; Rivera-Carrillo, M.; Raptis, R. G., *Inorg. Chim. Acta,* **2004**, 357, 3721-3732.
80. Mezei, G.; Rivera-Carrillo, M.; Raptis, R. G., *Dalton Trans.,* **2007**, 37-40.
81. Casarin, M.; Cingolani, A.; Di Nicola, C.; Falcomer, D.; Monari, M.; Pandolfo, L.; Pettinari, C., *Cryst. Growth Des.,* **2007**, 7, 676-685.
82. Casarin, M.; Corvaja, C.; Di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F., *Inorg. Chem.,* **2005**, 44, 6265-6276.
83. Casarin, M.; Corvaja, C.; di Nicola, C.; Falcomer, D.; Franco, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Piccinelli, F.; Tagliatesta, P., *Inorg. Chem.,* **2004**, 43, 5865-5876.
84. Di Nicola, C.; Garau, F.; Karabach, Y. Y.; Martins, L.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A. J. L., *Eur. J. Inorg. Chem.,* **2009**, 666-676.
85. Di Nicola, C.; Karabach, Y. Y.; Kirillov, A. M.; Monari, M.; Pandolfo, L.; Pettinari, C.; Pombeiro, A. J. L., *Inorg. Chem.,* **2007**, 46, 221-230.
86. Hulsbergen, F. B.; Tenhoedt, R. W. M.; Verschoor, G. C.; Reedijk, J.; Spek, A. L., *J. Chem. Soc.-Dalton Trans.,* **1983**, 539-545.
87. Liu, X. M.; de Miranda, M. P.; McInnes, E. J. L.; Kilner, C. A.; Halcrow, M. A., *Dalton Trans.,* **2004**, 59-64.
88. Rivera-Carrillo, M.; Chakraborty, I.; Mezei, G.; Webster, R. D.; Raptis, R. G., *Inorg. Chem.,* **2008**, 47, 7644-7650.
89. Zhou, J. H.; Liu, Z.; Li, Y. Z.; Song, Y.; Chen, X. T.; You, X. Z., *J. Coord. Chem.,* **2006**, 59, 147-156.
90. Angaroni, M.; Ardizzoia, G. A.; Beringhelli, T.; La Monica, G.; Gatteschi, D.; Masciocchi, N.; Moret, M., *J. Chem. Soc.-Dalton Trans.,* **1990**, 3305-3309.
91. Shen, W. Z.; Yi, L.; Cheng, P.; Yan, S. P.; Liao, D. Z.; Jiang, Z. H., *Inorg. Chem. Commun.,* **2004**, 7, 819-822.
92. Dias, H. V. R.; Diyabalanage, H. V. K.; Gamage, C. S. P., *Chem. Commun.,* **2005**, 1619-1621.
93. Sakai, K.; Yamada, Y.; Tsubomura, T.; Yabuki, M.; Yamaguchi, M., *Inorg. Chem.,* **1996**, 35, 542-544.
94. Kogane, T.; Yamamoto, T.; Hayashi, M.; Hirota, R.; Horiuchi, C. A., *Polyhedron,* **1995**, 14, 2475-2482.
95. Kavlakoglu, E.; Elmali, A.; Elerman, Y.; Svoboda, I., *Polyhedron,* **2002**, 21, 1539-1545.
96. Manzur, J.; García, A. M.; Garland, M. T.; Acuna, V.; González, O.; Peña, O.; Atria, A. M.; Spodine, E., *Polyhedron,* **1996**, 15, 821-827.
97. Mokuolu, Q. F.; Foguet-Albiol, D.; Jones, L. F.; Wolowska, J.; Kowalczyk, R. M.; Kilner, C. A.; Christou, G.; McGowan, P. C.; Halcrow, M. A., *Dalton Trans.,* **2007**, 1392-1399.
98. Sanz, M.; Mosquera, M. E. G.; Cuenca, T., *Dalton Trans.,* **2009**, 2616-2622.
99. Umakoshi, K.; Kojima, T.; Arikawa, Y.; Onishi, M., *Chem.-Eur. J.,* **2006**, 12, 5094-5104.
100. Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J., *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.,* **1994**, 50, 1023-1026.

101. Kruger, P. E.; Launay, F.; McKee, V., *Chem. Commun.,* **1999**, 639-640.
102. Liu, X. M.; McAllister, J. A.; de Miranda, M. P.; Whitaker, B. J.; Kilner, C. A.; Thornton-Pett, M.; Halcrow, M. A., *Angew. Chem.-Int. Edit.,* **2002**, 41, 756-758.
103. Liu, X. M.; McAllister, J. A.; de Miranda, M. P.; McInnes, E. J. L.; Kilner, C. A.; Halcrow, M. A., *Chem.-Eur. J.,* **2004**, 10, 1827-1837.
104. Liu, X. M.; McLaughlin, A. C.; de Miranda, M. P.; McInnes, E. J. L.; Kilner, C. A.; Halcrow, M. A., *Chem. Commun.,* **2002**, 2978-2979.
105. Merz, L.; Haase, W., *J. Chem. Soc.-Dalton Trans.,* **1980**, 875-879.
106. Raptis, R. G.; Georgakaki, I. P.; Hockless, D. C. R., *Angew. Chem.-Int. Edit.,* **1999**, 38, 1632-1634.
107. Baran, P.; Boča, R.; Chakraborty, I.; Giapintzakis, J.; Herchel, R.; Huang, Q.; McGrady, J. E.; Raptis, R. G.; Sanakis, Y.; Simopoulos, A., *Inorg. Chem.,* **2008**, 47, 645-655.
108. Capparelli, M. V.; Hodge, P.; Piggott, B., *Chem. Commun.,* **1997**, 937-938.
109. Ehlert, M. K.; Rettig, S. J.; Storr, A.; Thompson, R. C.; Trotter, J., *Inorg. Chem.,* **1993**, 32, 5176-5182.
110. Wu, H. Z.; Li, H. X.; Cheng, M. L.; Zhang, W. H.; Zhang, Y.; Lang, H. P., *Inorg. Chem. Commun.,* **2008**, 11, 8-10.
111. Xu, J. Y.; Qiao, X.; Song, H. B.; Yan, S. P.; Liao, D. Z.; Gao, S.; Journaux, Y.; Cano, J., *Chem. Commun.,* **2008**, 6414-6416.
112. Chandrasekhar, V.; Kingsley, S., *Angew. Chem.-Int. Edit.,* **2000**, 39, 2320-2322.
113. Kruger, P. E.; Moubaraki, B.; Fallon, G. D.; Murray, K. S., *J. Chem. Soc.-Dalton Trans.,* **2000**, 713-718.
114. He, J.; Yin, Y. G.; Wu, T.; Li, D.; Huang, X. C., *Chem. Commun.,* **2006**, 2845-2847.
115. Yu, S. Y.; Huang, H. P.; Li, S. H.; Jiao, Q.; Li, Y. Z.; Wu, B.; Sei, Y.; Yamaguchi, K.; Pan, Y. J.; Ma, H. W., *Inorg. Chem.,* **2005**, 44, 9471-9488.
116. Zhang, J. P.; Horike, S.; Kitagawa, S., *Angew. Chem.-Int. Edit.,* **2007**, 46, 889-892.
117. Zhang, J. P.; Kitagawa, S., *J. Am. Chem. Soc.,* **2008**, 130, 907-917.
118. La Monica, G.; Ardizzoia, G. A., *Progr. Inorg. Chem.,* **1997**, 46, 151-238.
119. Ackermann, J.; Meyer, F.; Pritzkow, H., *Z. Anorg. Allg. Chem.,* **2004**, 630, 2627-2631.
120. Bauer-Siebenlist, B.; Dechert, S.; Meyer, F., *Chem.-Eur. J.,* **2005**, 11, 5343-5352.
121. Bauer-Siebenlist, B.; Meyer, F.; Farkas, E.; Vidovic, D.; Cuesta-Seijo, J. A.; Herbst-Irmer, R.; Pritzkow, H., *Inorg. Chem.,* **2004**, 43, 4189-4202.
122. Bauer-Siebenlist, B.; Meyer, F.; Vidovic, D.; Pritzkow, H., *Z. Anorg. Allg. Chem.,* **2003**, 629, 2152-2156.
123. Demeshko, S.; Leibeling, G.; Dechert, S.; Fuchs, S.; Pruschke, T.; Meyer, F., *ChemPhysChem,* **2007**, 8, 405-417.
124. Demeshko, S.; Leibeling, G.; Dechert, S.; Meyer, F., *Dalton Trans.,* **2006**, 3458-3465.
125. Demeshko, S.; Leibeling, G.; Maringgele, W.; Meyer, F.; Mennerich, C.; Klauss, H. H.; Pritzkow, H., *Inorg. Chem.,* **2005**, 44, 519-528.
126. Leibeling, G.; Demeshko, S.; Bauer-Siebenlist, B.; Meyer, F.; Pritzkow, H., *Eur. J. Inorg. Chem.,* **2004**, 2413-2420.
127. Meyer, F.; Demeshko, S.; Leibeling, G.; Kersting, B.; Kaifer, E.; Pritzkow, H., *Chem.-Eur. J.,* **2005**, 11, 1518-1526.
128. Meyer, F.; Kircher, P.; Pritzkow, H., *Chem. Commun.,* **2003**, 774-775.
129. Meyer, F.; Konrad, M.; Kaifer, E., *Eur. J. Inorg. Chem.,* **1999**, 1851-1854.
130. Meyer, F.; Pritzkow, H., *Angew. Chem.-Int. Edit.,* **2000**, 39, 2112-2115.
131. Meyer, F.; Ruschewitz, U.; Schober, P.; Antelmann, B.; Zsolnai, L., *Dalton Trans.,* **1998**, 1181-1186.
132. Meyer, F.; Winter, R. F.; Kaifer, E., *Inorg. Chem.,* **2001**, 40, 4597-4603.
133. Prokofieva, A.; Prikhod'ko, A. I.; Enyedy, E. A.; Farkas, E.; Maringgele, W.; Demeshko, S.; Dechert, S.; Meyer, F., *Inorg. Chem.,* **2007**, 46, 4298-4307.
134. Stollenz, M.; Gross, C.; Meyer, F., *Chem. Commun.,* **2008**, 1744-1746.
135. Hou, J. Z.; Li, M.; Li, Z.; Zhan, S. Z.; Huang, X. C.; Li, D., *Angew. Chem.-Int. Edit.,* **2008**, 47, 1711-1714.

136. Yoneda, K.; Adachi, K.; Nishio, K.; Yamasaki, M.; Fuyuhiro, A.; Katada, M.; Kaizaki, S.; Kawata, S., *Angew. Chem.-Int. Edit.,* **2006**, 45, 5459-5461.
137. Chandrasekhar, V.; Kingsley, S.; Vij, A.; Lam, K. C.; Rheingold, A. L., *Inorg. Chem.,* **2000**, 39, 3238-3242.
138. Hu, T. L.; Li, J. R.; Liu, C. S.; Shi, X. S.; Zhou, J. N.; Bu, X. H.; Ribas, J., *Inorg. Chem.,* **2006**, 45, 162-173.
139. Jeffery, J. C.; Jones, P. L.; Mann, K. L. V.; Psillakis, E.; McCleverty, J. A.; Ward, M. D.; White, C. M., *Chem. Commun.,* **1997**, 175-176.
140. Jones, P. L.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D., *Polyhedron,* **1997**, 16, 1567-1571.
141. Mann, K. L. V.; Psillakis, E.; Jeffery, J. C.; Rees, L. H.; Harden, N. M.; McCleverty, J. A.; Ward, M. D.; Gatteschi, D.; Totti, F.; Mabbs, F. E.; McInnes, E. J. L.; Riedi, P. C.; Smith, G. M., *J. Chem. Soc.-Dalton Trans.,* **1999**, 339-348.
142. Picart, J. P.; Sánchez, F. J.; Casabó, J.; Rius, J.; Alvarez-Larena, A.; Ros, J., *Inorg. Chem. Commun.,* **2002**, 5, 130-133.
143. Pons, J.; Sanchez, F. J.; Casabó, J.; Alvarez-Larena, A.; Piniella, J. F.; Ros, J., *Inorg. Chem. Commun.,* **2003**, 6, 833-836.
144. Singh, K. J.; Long, J. R.; Stavropoulos, P., *Inorg. Chem.,* **1998**, 37, 1073-1079.
145. van der Vlugt, J. I.; Demeshko, S.; Dechert, S.; Meyer, F., *Inorg. Chem.,* **2008**, 47, 1576-1585.
146. Chandrasekhar, V.; Nagarajan, L.; Gopal, K.; Baskar, V.; Kogerler, P., *Dalton Trans.,* **2005**, 3143-3145.
147. Jones, L. F.; Kilner, C. A.; Halcrow, M. A., *Polyhedron,* **2007**, 26, 1977-1983.
148. Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E., *Inorg. Chem.,* **1976**, 15, 2107-2110.
149. Zhou, Y.; Chen, W., *Dalton Trans.,* **2007**, 5123-5125.
150. Aromí, G.; Bell, A.; Teat, S. J.; Whittaker, A. G.; Winpenny, R. E. P., *Chem. Commun.,* **2002**, 1896-1897.
151. Dearden, A. L.; Parsons, S.; Winpenny, R. E. P., *Angew. Chem.-Int. Edit.,* **2001**, 40, 151-154.
152. Aromí, G.; Bell, A. R.; Helliwell, M.; Raftery, J.; Teat, S. J.; Timco, G. A.; Roubeau, O.; Winpenny, R. E. P., *Chem.-Eur. J.,* **2003**, 9, 3024-3032.
153. Aromí, G.; Roubeau, O.; Helliwell, M.; Teat, S. J.; Winpenny, R. E. P., *Dalton Trans.,* **2003**, 3436-3442.
154. Aromí, G.; Bell, A.; Teat, S. J.; Winpenny, R. E. P., *Chem. Commun.,* **2005**, 2927-2929.
155. Bell, A.; Aromí, G.; Teat, S. J.; Wernsdorfer, W.; Winpenny, R. E. P., *Chem. Commun.,* **2005**, 2808-2810.
156. Liu, C. M.; Zhang, D. Q.; Zhu, D. B., *Chem. Commun.,* **2008**, 368-370.
157. Liu, C. M.; Zhang, D. Q.; Zhu, D. B., *Inorg.Chem.,* **2009**.
158. King, P.; Clerac, R.; Anson, C. E.; Coulon, C.; Powell, A. K., *Inorg. Chem.,* **2003**, 42, 3492-3500.
159. King, P.; Clerac, R.; Anson, C. E.; Powell, A. K., *Dalton Trans.,* **2004**, 852-861.
160. Xing, Y. H.; Zhou, G. H.; An, Y.; Zeng, X. Q.; Ge, M. F., *Synth. React. Inorg. Met.-Org. Nano-Metal Chem.,* **2008**, 38, 514-517.
161. Zhou, X. H.; Peng, Y. H.; Du, X. D.; Wang, C. F.; Zuo, J. L.; You, X. Z., *Cryst. Growth Des.,* **2009**, 9, 1028-1035.
162. Driessen, W. L.; Chang, L.; Finazzo, C.; Gorter, S.; Rehorst, D.; Reedijk, J.; Lutz, M.; Spek, A. L., *Inorg. Chim. Acta,* **2003**, 350, 25-31.
163. Angaroni, M.; Ardizzoia, G. A.; La Monica, G.; Beccalli, E. M.; Masciocchi, N.; Moret, M., *J. Chem. Soc.-Dalton Trans.,* **1992**, 2715-2721.
164. Zhang, H.; Fu, D. G.; Ji, F.; Wang, G. X.; Yu, K. B.; Yao, T. Y., *J. Chem. Soc.-Dalton Trans.,* **1996**, 3799-3803.
165. Klingele, J.; Prikhod'ko, A. I.; Leibeling, G.; Demeshko, S.; Dechert, S.; Meyer, F., *Dalton Trans.,* **2007**, 2003-2013.
166. Kovbasyuk, L.; Pritzkow, H.; Kramer, R.; Fritsky, I. O., *Chem. Commun.,* **2004**, 880-881.
167. Kramer, R.; Fritsky, I. O.; Pritzkow, H.; Kovbasyuk, L. A., *J. Chem. Soc.-Dalton Trans.,* **2002**, 1307-1314.

168. Noel, G.; Roder, J. C.; Dechert, S.; Pritzkow, H.; Bolk, L.; Mecking, S.; Meyer, F., *Adv. Synth. Catal.,* **2006**, 348, 887-897.
169. Roder, J. C.; Meyer, F.; Pritzkkow, H., *Chem. Commun.,* **2001**, 2176-2177.
170. Sachse, A.; Noël, G.; Dechert, S.; Demeshko, S.; Honecker, A.; Alfonsov, A.; Kataev, V.; Meyer, F., *Eur. J. Inorg. Chem.,* **2008**, 5390-5396.
171. Shindo, K.; Mori, Y.; Motoda, K.; Sakiyama, H.; Matsumoto, N.; Okawa, H., *Inorg. Chem.,* **1992**, 31, 4987-4990.
172. Konrad, M.; Wuthe, S.; Meyer, F.; Kaifer, E., *Eur. J. Inorg. Chem.,* **2001**, 2233-2240.
173. Penkova, L.; Demeshko, S.; Haukka, M.; Pavlenko, V. A.; Meyer, F.; Fritsky, I. O., *Z. Anorg. Allg. Chem.,* **2008**, 634, 2428-2436.
174. Pal, S.; Barik, A. K.; Gupta, S.; Hazra, A.; Kar, S. K.; Peng, S. M.; Lee, G. H.; Butcher, R. J.; El Fallah, M. S.; Ribas, J., *Inorg. Chem.,* **2005**, 44, 3880-3889.
175. Gale, P. A., *Coord. Chem. Rev.,* **2000**, 199, 181-233.
176. Schmidtchen, F. P.; Berger, M., *Chem. Rev.,* **1997**, 97, 1609-1646.
177. Pecoraro, V. L.; Stemmler, A. J.; Gibney, B. R.; Bodwin, J. J.; Wang, H.; Kampf, J. W.; Barwinski, A., *Prog. Inorg. Chem.,* **1997**, 45, 83-177.
178. Lehn, J. M., *Angew. Chem.-Int. Edit. Engl.,* **1988**, 27, 89-112.
179. Escartí, F.; Miranda, C.; Lamarque, L.; Latorre, J.; García-España, E.; Kumar, M.; Arán, V. J.; Navarro, P., *Chem. Commun.,* **2002**, 936-937.
180. Mezei, G.; Baran, P.; Raptis, R. G., *Angew. Chem.-Int. Edit.,* **2004**, 43, 574-577.
181. Mohamed, A. A.; Burini, A.; Galassi, R.; Paglialunga, D.; Galán-Mascarós, J. R.; Dunbar, K. R.; Fackler, J. P., *Inorg. Chem.,* **2007**, 46, 2348-2349.
182. Puerta, D. T.; Cohen, S. M., *Chem. Commun.,* **2003**, 1278-1279.
183. Jones, L. F.; Barrett, S. A.; Kilner, C. A.; Halcrow, M. A., *Chem.-Eur. J.,* **2008**, 14, 223-233.
184. Jones, L. F.; Kilner, C. A.; De Miranda, M. P.; Wolowska, J.; Halcrow, M. A., *Angew. Chem.-Int. Edit.,* **2007**, 46, 4073-4076.
185. Jones, L. F.; Kilner, C. A.; Halcrow, M. A., *Chem.-Eur. J.,* **2009**, 15, 4667-4675.
186. Albrecht, M., *Chem. Rev.,* **2001**, 101, 3457-3497.
187. Piguet, C.; Bernardinelli, G.; Hopfgartner, G., *Chem. Rev.,* **1997**, 97, 2005-2062.