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Magnetic and spectroscopic studies of iron and manganese complexes

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CHAPTER 1

From Cyanide Complexes as Functional Components in Magnetic Materials

This chapter gives an overview on metal cyanide complexes. The properties of mononuclear cyanide complexes are described and their uses as building blocks in the formation of bimetallic systems, i.e. Prussian Blue Analogs (PBAs), are focused upon. The motivation for studying PBAs is their potentially interesting photo and magnetic properties.

1.1- The cyano group

The cyano (or cyanide) group refers to the CN^- functionality in which the carbon and nitrogen atoms are connected to each other through a triple bond. When present in organic molecules as a functional group, it is referred to as a nitrile; the synthesis of the first nitrile from formic acid and hydrogen cyanide was reported by C.W. Scheele in 1782.¹ In inorganic compounds, cyano-containing molecules are referred to as “cyanides”. The oldest reaction is that of Fe^{2+} with CN^- from ferrous sulfate and KCN, respectively; in which bonding is extremely strong (Fe-CN bond). This reaction was reported as one of the steps in the synthesis of the dye Prussian blue in 1704.

Although in itself cyanide is highly toxic, its use as a ligand in the synthesis of coordination compounds has led to a wide area of research, from dyes, to electron transfer and in magnetic materials. From the spectrochemical series²: $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{bipy} < \text{NO}^{2-} < \text{CN}^- \sim \text{CO}$, the carbon-bonded cyanide is located at the strong field limit whereas the field strength of the nitrogen-bonded cyanide is below that of ammonia. The chemistry of cyanide compounds is of contemporary relevance; the ditopic character of cyanide as a ligand raises the possibility of it being used either as a monodentate ligand in the synthesis of the mononuclear complexes M-CN (M = metal ion) or as a bridging ligand in the synthesis of binuclear complexes $\text{M-CN-M}'$ (M' = metal ion) from the reaction of a mononuclear compound with another metal ion via the nitrogen atom. The high affinity of cyanide for metal ions results in the formation of complexes, either mononuclear or binuclear, which possess interesting physical and chemical properties with respect to applications.

1.2- Mononuclear cyanides complexes

A large number of metal cyanides of the type M-CN have already been reported with $\text{M} = \text{Fe}^{2+/3+}$, Co^{3+} , Mn^{3+} , Ru^{2+} , Os^{2+} and Cr^{3+} .^{3,4} Typically in an octahedral environment, these transition metal ions coordinate six cyano ligands to form $[\text{M}(\text{CN})_6]^{3-/4-}$ species. Some of these complexes have also been reported for the second and third row transition metal ions with eight cyano ligands $[\text{Mo}(\text{CN})_8]$ and $[\text{W}(\text{CN})_8]$, respectively.^{5,6}

The oldest and most widely used complex is $[\text{Fe}(\text{CN})_6]^{3-/4-}$. Apart from the fact that a series of synthesized hexacyanometallate analogues have been reported with different metals, a more relevant aspect of the compound $[\text{Fe}(\text{CN})_6]^{2-/3-}$ is the possible substitution of one of the cyano ligands to form the pentacyano ferrate complex of the type $[\text{Fe}(\text{CN})_5\text{L}]^{2-/3-}$ (L is a different ligand). The ligand L is non-innocent and therefore modifies and adds new properties to the complex. Several complexes of this type with a wide range of ligands L have been reported with sodium nitroprusside ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$) being one of the most extensively studied pentacyanoferrate complex.⁷

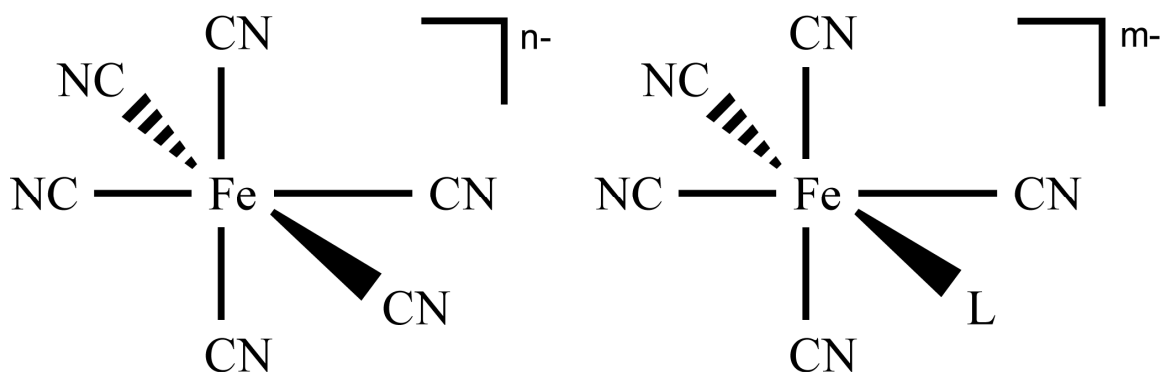


Figure 1.1: Spatial representation of the $[\text{Fe}(\text{CN})_6]^{n-}$ and $[\text{Fe}(\text{CN})_5\text{L}]^{m-}$ compounds.

These compounds have been isolated with different counter-cations such as potassium, sodium or even an organic counterion such as guanidinium (CN_3H_6),⁸ tetra-, tri- or diphenylphosphonium (Ph_4P^+ , MePh_3P^+ , $\text{Me}_2\text{Ph}_2\text{P}^+$),⁹ tetrabutylammonium¹⁰ or tetramethylammonium.¹¹

1.2.1- Synthesis

Synthesis of $\text{Fe}(\text{CN})_6$ complex

The hexacyanoferrate(II) or hexacyanoferrate(III) ions are isolated from the reaction of a stoichiometric proportion of a chloride or sulphate salt of iron(II or III) with potassium cyanide (KCN) or sodium cyanide (NaCN) depending on the counter-cation required.

Synthesis of $[\text{Fe}^{\text{II,III}}(\text{CN})_5\text{L}]^{m-}$ compounds

A number of procedures can be used to synthesize $[\text{Fe}(\text{CN})_5\text{L}]^{m-}$ compounds.

Direct preparation from a mixture of a stoichiometric amount of an aqueous solution of Fe^{II} with a cyanide salt such ACN (A = K or Na) under an atmosphere of CO leads to the

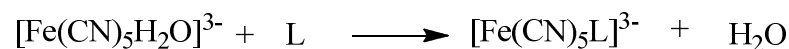
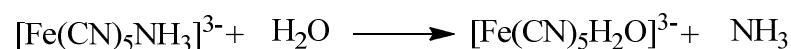
formation of the $\text{Na}_3[\text{Fe}(\text{CN})_5\text{CO}]$ complex.¹² By following the same procedure $[\text{Et}_4\text{N}]_3[\text{Fe}^{\text{II}}(\text{CN})_5(\text{py})]$ can be obtained from the reaction of FeCl_2 with five equivalents of CN in pyridine.

It is possible to substitute one of the cyano ligands of the hexacyanoferrate anion $[\text{Fe}(\text{CN})_6]^{n-}$ with a different ligand. This is the case for $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, also called nitroprusside, which is extracted from a mixture of an aqueous solution of $[\text{Fe}(\text{CN})_6]^{3-}$ with nitric acid.¹³ Under high temperature and pressure $\text{Na}_3[\text{Fe}(\text{CN})_5\text{CO}]$ is formed from the reaction of CO and $[\text{Fe}(\text{CN})_6]^{4-}$.¹⁴

However, the vast majority of the $[\text{Fe}^{\text{II,III}}(\text{CN})_5(\text{L})]^{n-}$ compounds have been obtained by a multistep reaction sequence. The preparation of which involves a series of ligand exchange reactions at the iron center, which starts with the nitric acid oxidation of $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ to form the nitroprusside anion ($[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$). This is followed by a displacement reaction of the NO ligand by NH_3 via an oxido-reduction reaction between excess ammonia and sodium nitroprusside to form the pentacyanoaminoferrate complex ($[\text{Fe}(\text{CN})_5\text{NH}_3]^{3-}$).¹⁵



Finally, many other $\text{Na}_3[\text{Fe}(\text{CN})_5\text{L}]$ complexes can be isolated from solution by using the $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ as precursor in which the amine ligand NH_3 is substituted by another ligand L.^{15,16,17} Since many of these substitution reactions take place in aqueous media, an intermediate unstable complex $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ is formed in situ during the process as represented in the equations below.



All of these synthetic methods apply to the ferrous complexes; the ferric complexes are formed from the oxidation of the corresponding ferrous complexes. Hydrogen peroxide (H_2O_2) or potassium periodate (KIO_4) can be used as oxidant¹⁸ to prepare the ferric complex $[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}]^{2-}$ from its ferrous state in situ. Subsequent air oxidation produces the ferric complex $[(n\text{-Bu})_4\text{N}]_2[\text{Fe}^{\text{III}}(\text{CN})_5(\text{py})]$ from its ferrous complex.¹⁹

1.2.2- Characterization

The pentacyanoferrate complexes are generally hydrated except for some of the alkali nitroprussides with larger cations such as Rb^+ and Cs^+ (RbNP , CsNP), which crystallize as anhydrous salts.²⁰

Although various substituted pentacyano(L)ferrate complexes have been synthesized, only a few have been characterized structurally.^{21,22} These complexes have an octahedral structure with interatomic iron-L distances that depend on the oxidation state of the metal as in the case of $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 7\text{H}_2\text{O}$ where the $\text{Fe}^{\text{II}}\text{-N}$ distance²³ is 0.06 Å longer than the $\text{Fe}^{\text{III}}\text{-N}$ distance²⁴ in Fe^{III} analogues. Depending on the electron-withdrawing or donating ability of L, its coordination to the pentacyanoferrate complex can modify the octahedral structure of the complex such that the *trans*-Fe-C distance will differ from the *cis*-Fe-C distance.

Mössbauer and infrared spectroscopic studies on a series of substituted sodium pentacyano ferrate(II) complexes reported by Brar and Mazumdar²⁵ reveal that the quadrupole splitting (ΔE_Q) is affected by both the substituted L and the cyano ligand CN^- *trans* to it, $[\text{Fe}(\text{CN})_5\text{L}]$, such that ΔE_Q increases when L is a better π -acceptor or less effective σ -donor than CN^- ; in the order $\text{enH}^+ < \text{N}_2\text{H}_5^+ < \text{NH}_3 < \text{H}_2\text{O} < \text{NO}_2^- < \text{NO}^+$ (enH^+ is protonated ethylenediamine). The reverse order is applicable for the isomer shift.

Cyanide can act as a σ -donor (by donating electrons to a metal) and π -acceptor (by accepting electrons from a metal) with the σ -donor ability being dominating its π -acceptor ability because of its negative charge. σ -Donation also increases with the removal of electrons from the weakly antibonding σ molecular orbital and therefore increases the ν_{CN} value while conversely its π -accepting properties decrease with the addition of electrons into the π bonding orbital and therefore a decrease of ν_{CN} is observed.

One of the main vibrational characteristics of the pentacyanoferrate is the CN vibrational modes. ν_{CN} stretching vibrations are dependent on the cyano ligands' environment. The ν_{CN} bands of Fe-CN appear in the region between 2000 and 2100 cm^{-1} when the cyano is bonded to the Fe^{II} ion center. These bands shift to higher frequencies (between 2100 and 2200 cm^{-1}) upon oxidation of the metal center to the Fe^{III} state due to the decrease in the π -acceptance of the CN^- ligand.

The number of bands allows for the symmetry of the compound to be ascertained. Although the structure of the $[\text{Fe}(\text{CN})_5\text{L}]^{m-}$ is generally distorted and hence has reduced

symmetry, the assignment of bands are mainly based on the assumption of C_{4v} symmetry. The anion nitroprusside $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ in the form $\text{Ti}_2[\text{Fe}(\text{CN})_5\text{NO}]$ shows four IR bands in the CN stretching region, where modes at 2146 and 2140 cm^{-1} are assigned to A_1 , 2134 cm^{-1} assigned to B_1 and 2122 cm^{-1} assigned to E .²⁶ These values are about 30 cm^{-1} lower compared to those of sodium nitroprusside²⁷ and about 10 cm^{-1} lower than those reported for $\text{Rb}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot \text{H}_2\text{O}$,²⁸ showing the importance of counterion to the properties of the complex.

The ν_{CN} stretching frequency of this series of pentacyanoferrate(II) complexes was also found to decrease with the order $\text{NO}^+ < \text{NO}_2^- < \text{N}_2\text{H}_5^+ < \text{enH}^+ \approx \text{NH}_3$; the decrease in the frequency correlates with the increase in the isomer shift.

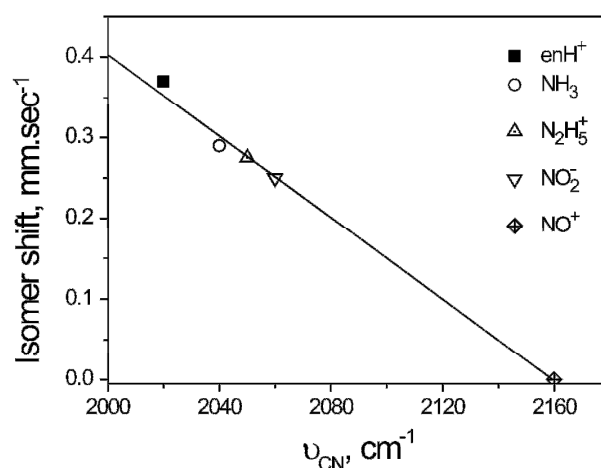


Figure 1.2: Representation of variation of the isomer shift versus the asymmetric stretching frequency ν_{CN} of $[\text{Fe}(\text{CN})_5\text{L}]^m$. (Reproduced from reference 25).

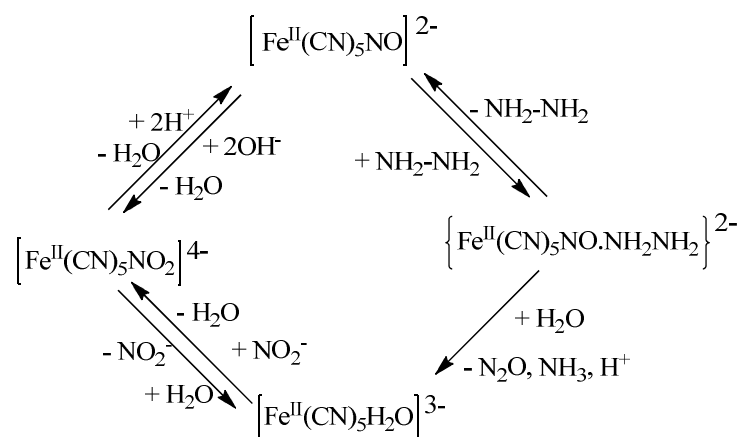
The pentacyano(L)ferrate(II) complexes (with L being an aromatic ligand) exhibit an intense metal to ligand charge transfer (MLCT) band²⁹ in the visible to near UV region of the spectrum. Shepherd et al. have shown that the origin of the ligand-to-metal charge-transfer bands observed for the low-spin $d^5 \text{Fe}^{\text{III}}$ (from $[\text{Fe}(\text{CN})_5\text{L}]^{2-}$ and L = imidazole, pyrazole or their derivatives) appear in the visible and UV regions and could be assigned on the basis of the HOMOs of L. These bands shift to lower energy upon deprotonation of the ligand.³⁰

A spectrochemical order for back-donation of pentacyano-complexes of Fe(II) with aromatic nitrogen heterocycles prepared by Toma et al. was shown to be *N*-methylpyrazinium > pyrazine ~ isonicotinamide > pyridine > 4-methylpyridine, for the correlation of electron-transfer energy with the energy of the unoccupied orbitals in the aromatic nitrogen heterocyclic ligands.³¹

1.2.3- Uses of cyanoferrate complexes.

Mixed iron(II) cyanide complexes can be treated as precursors in catalyzed redox reactions. Kamaluddin et al. reported a series of $[\text{Fe}(\text{CN})_5\text{L}]^{3-/4-}$ anions (with L = glycine, histidine, imidazole or triglycine) as catalyst in the decomposition of hydrogen peroxide.³² During the reaction, L is substituted with an hydroxide ion and the newly formed complex reacts with the hydrogen peroxide to form an unstable intermediate. The rate of the reaction is controlled by the decomposition of the precursor complex.

Evidence for the catalytic properties of the $[\text{Fe}(\text{CN})_5\text{L}]^{3-}$ ion has been reported by Chevalier et al. in the reduction of nitrite by hydrazine as represented in scheme 1.1. Nucleophilic attack of the hydrazine leads to the formation of the N_2O , NH_3 and $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ ions.³³ The aqua complex binds more nitrite, which converts to NO^+ upon coordination and enters a new cycle.



Scheme 1.1: Catalytic cycle for the reduction of nitrite by hydrazine.³⁴

$[\text{Fe}^{\text{II}}(\text{CN})_5\text{NO}]^{2-}$ was also reported to catalyze the auto-oxidation of cysteine to cystine³⁵ involving the NO^+/NO redox couple with dioxygen as terminal oxidant. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ (SNP) is the most investigated system.³⁶ Under laser irradiation at low temperature the nitroprusside anion $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ displays a metastable state which arises from the $7^e(\pi^*\text{NO}) \leftarrow 2b_2(d_{xy})$.^{37,38} The two metastable states SI and SII of the SNP, which decay at about 198 K and 147 K, respectively, are separated from the ground state by potential energy barriers of 0.7 eV and 0.5 eV, respectively.³⁹ Excitation can take place under irradiation with light in the spectral range of 350-580 nm and the deactivation to the ground state occurs upon irradiation between of 600-1200 nm or by increasing the temperature. This long-living metastable state gives sodium nitroprusside (SNP) as well as the barium salt $\text{Ba}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$ ⁴⁰ potential for use as an optical-memory storage

material.⁴¹ Because of its NO-donor ability, SNP has also been explored widely for pharmaceutical applications due to the biological properties of NO (*i.e.* lowering blood pressure).^{42, 43, 44}

One of the most important properties of the mononuclear cyanometallate complexes is their use as starting material in the synthesis of bimetallic cyanide complexes in which, due to the ditopic ability of the cyano ligand, the two metal centers are bonded through the carbon and the nitrogen of the cyanide ligand, M-CN-M' (M and M' are any transition metal ion).

1.3- Bimetallic cyanide compounds.

1.3-1 Synthesis

By reacting $[\text{Fe}(\text{CN})_6]^{3-}$ with an aqueous solution of Fe^{2+} a deep blue complex called *Turnbull's Blue* is formed while the reaction of $[\text{Fe}(\text{CN})_6]^{4-}$ with an aqueous solution of Fe^{3+} ions forms a deep blue complex called *Prussian Blue*; in both case the complexes formed are hydrated salts and of the formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ (with $x \approx 14$)⁴⁵ with blue color due to the inter valence transition between Fe(II) and Fe(III) sites. This was accidentally discovered for the first time in 1704 by a Berliner draper M. Diesbach.⁴⁶ The structure was proposed by Keggin and Miles⁴⁷ and later reformulated by Ludi and Güdel.⁴⁸ Since then, based on this formula, by substituting the center or counter metal ion with any other transition metal ions a wide family of Prussian blue complexes have been synthesized of general formula $\text{A}_n\text{M}_a[\text{M}'(\text{CN})_6]_b \cdot x\text{H}_2\text{O}$, called Prussian blue analogues (PBAs) (where M^{m+} and M'^{p+} are any transition metal ions, A^+ is an alkali cation). These binuclear compounds form three-dimensional structures such that the cyano (CN^-) acts as a bridging ligand and both metal ions are in an octahedral environment. The arrangement of atoms form a cubic system where M^{m+} ions occupy all the corners and the centers of the faces while the $[\text{M}'(\text{CN})_6]^{n-}$ ions occupy the octahedral sites and the cations A^+ can be located in part of the tetrahedral sites of the cubic system. The cell parameter of the cubic structure of the PBAs varies between 10.0 and 10.9 Å.⁴⁹

According to the stoichiometry of the metal ions and the presence or absence of the alkali metal, three main structures have been identified as represented in figures 1.3 below. The ratio M/M' can be 1:1 in the case of trivalent metal ions $\text{M}(\text{III})[\text{M}'(\text{III})(\text{CN})_6]$ or a mixture of bivalent and trivalent metal ions with an alkali ion $\text{A}(\text{I})\text{M}(\text{II})[\text{M}'(\text{III})(\text{CN})_6]$, the ratio

M/M' can also be 3:2 as in case of $M(II)_3[M'(III)(CN)_6]_2 \cdot xH_2O$. In figures 1.3 (b) and 1.3 (c) the octahedral environments are such that M' is bonded to six carbon atoms of cyanide whereas M is bonded to six nitrogen atoms of the cyanide ligand; however in the figure 1.3 (a) the centered metal ion M' is still connected to six cyanides through carbon but the counter metal M is coordinated to four nitrogen atoms and to two oxygen atoms of water molecules (MC_4O_2). These coordinated water molecules occupy the defects present in the structure due to the absence of some $[M'(CN)_6]$ molecules at the corresponding positions.

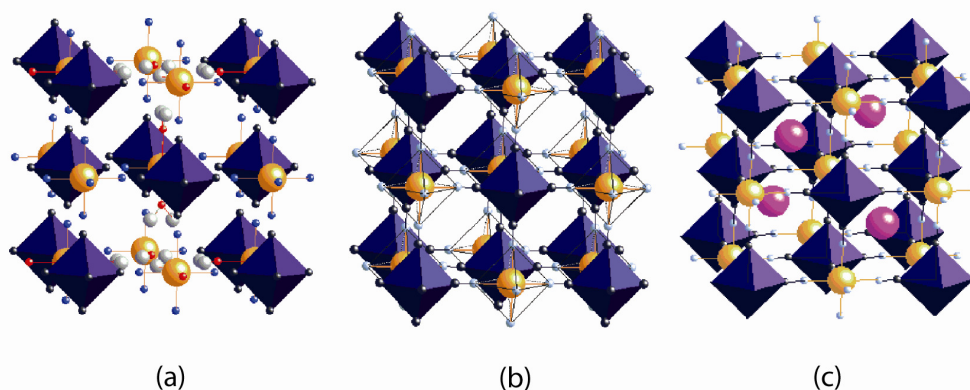


Figure 1.3: Cubic structure of Prussian blue analogues.⁵⁰ $M(II)_3[M'(III)(CN)_6]_2 \cdot xH_2O$ (a), $M(III)[M'(III)(CN)_6]$ (b), $A(I)M(II)[M'(III)(CN)_6]$ (c). Octahedra represent $[M'(CN)_6]$ moieties, light grey spheres represent M ions and dark gray spheres (when present) represent A ions. The water molecules in b) are represented by small spheres. (Reproduced with permission from reference 50).

These figures represent the three ideal structures of the PBAs that can be obtained but in reality, apart from a few reported structures,^{51,52} the PBAs are difficult to crystallize therefore their structural characterization is mostly limited to the resolution of their powder diffractograms and/or the elemental analysis. In most cases this reveals a non-stoichiometric formula which is an intermediate of the three ideal structures above.

Another series of PBAs have attracted considerable attention. By using the substituted pentacyano(L)ferrate complexes ($L = NO^+$, CO , NH_3 and H_2O) as building blocks, a new series of bimetallic complexes could be synthesized. These complexes were also reported to crystallize in three three-dimensional networks and in the cubic systems characteristic of Prussian Blue Analogues; however the space group is not $O_h^5-F_{m3m}$ in a strict sense because the symmetry group of the $[Fe(CN)_5L]^{3-}$ moiety⁵³ is not O_h but C_{4v} . In the case of the substituted pentacyanides, the channels formed result from the unbridged L ligand (replacing one of the cyanide) and also from the coordinated water molecules, which is unlikely in case of the hexacyanides for which the channels formed are from the

systematic $[\text{Fe}(\text{CN})_6]^{3-/4-}$ vacancies. The octahedral arrangement around the metal ion is not perfectly symmetric as in the case of the $\text{Mn}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$ or $\text{Cd}[\text{Fe}(\text{CN})_5\text{NO}] \cdot 3\text{H}_2\text{O}$.⁵⁴ The deformation of the distorted octahedral is manifested in the difference in the bond length $\text{Fe-N} = 1.667 \text{ \AA}$ that is shorter than the Fe-C bond length (1.942 \AA) and also the difference in electronegativity between the coordinated water molecule (lower) and the cyanide ligands (higher) cause deformation of the distorted octahedral array towards the coordinated water molecule.

1.3.2- Properties

The chemistry of the transition metal-cyanides has seen a remarkable revival in the past decade mostly due to interest in the magnetic and photomagnetic properties of bimetallic cyano-bridged molecules.

1.3.2.1- Magnetic properties

The complexes formed contained transition metals; therefore the five metal d orbitals (d_z^2 , d_{xy} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$) are involved. For these complexes, the d shell orbitals split into two subshell orbital energy levels; the separation of these orbitals depends on the geometry of the complex formed (Figure 1.4). In the octahedral structure, the orbitals split into two energy levels, one triply degenerate named t_{2g} (lower energy level containing d_{xy} , d_{xz} and d_{yz}) and one doubly degenerate named e_g (higher energy level containing d_z^2 and $d_{x^2-y^2}$). The inverse is the case for a tetrahedral structure.

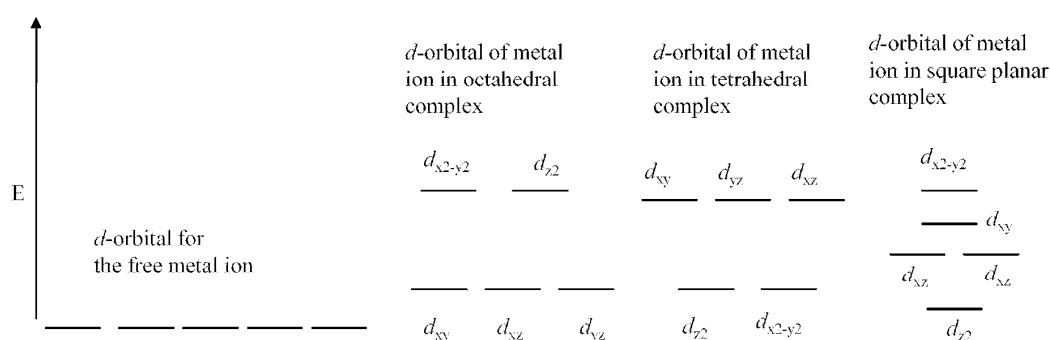


Figure 1.4: d -Orbital energy diagram.

Under an applied magnetic field the electric charge in a material can be field-induced to generate a magnetic moment opposed to the applied field. So the material can either be repelled in the case where all its electrons spins are paired (the material is said to be diamagnetic) or the material can be attracted in the case where it contains one or more

unpaired electrons (it is a paramagnetic material). In a ferromagnet, the magnetic moments of the contained unpaired electrons are oriented parallel to each other; by heating a ferromagnetic material, the magnetic moment are still parallel up to a Curie point (Figure 1.5) above which the material loses its ferromagnetic property to become a paramagnet. Unlike a ferromagnet, in an antiferromagnet these magnetic moments are oriented in opposite direction to each other.

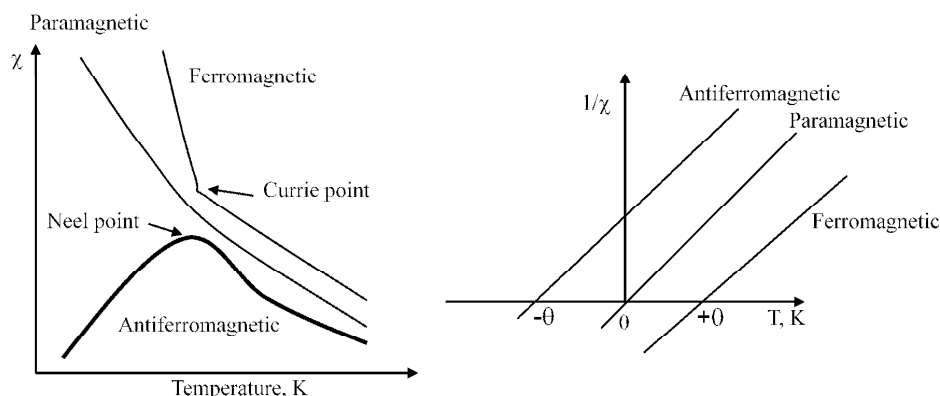


Figure 1.5: Representation of the variation of the magnetic susceptibility χ (left) and its reciprocal $1/\chi$ (right) versus temperature of a paramagnetic, ferromagnetic and antiferromagnetic material.

Since most of the PBAs are composed of transition metal ions, they contain d electrons. These metal ions can be diamagnetic in the case where all the electrons in d orbitals are paired. They can also be paramagnetic when they have one or more unpaired electrons in d orbitals.

Due to the field strength of the cyanide it can form low-spin state complexes through its carbon atom and high spin state complexes through its nitrogen atom; therefore in the binuclear system $M-NC-M'$, the central metal ion M' is surrounded by six carbons of the cyanides ($-NC-M'(CN)_5$), the strong ligand field induces a low spin metal center, whereas at the M site, the metal ion M is surrounded by a mixture of $6-x$ nitrogen atoms of the cyanide and x oxygen atoms ($[M(CN)_{6-x}(OH_2)_x]^{m-}$ with $x = 0-6$) depending on the stoichiometry of the material. These ligands are generally weak field therefore the metal ion M will be high spin. Since both metal centers are in an octahedral environment and the bridging character of the cyano ligand allows some magnetic interactions between metal ions, the entire molecule can be a paramagnet, ferromagnet or ferrimagnet. From the models developed by Hoffman⁵⁵ and Khan⁵⁶ to predict the nature of the exchange interaction, it was concluded that; the molecule is ferromagnetic if the orbitals of the metal centers bearing unpaired electrons are orthogonal and the molecule is antiferromagnetic when the orbitals overlap. According to the partition of electrons over the t_{2g} or e_g orbitals

on molecular-based magnets of bimetallic $(\text{CN})_5\text{-M}'\text{-CN-M}(\text{NC})_5$ complexes, three main situations might arise for the $\text{M}'\text{-M}$ interaction predictions.⁵⁰ When the magnetic orbitals t_{2g} of the M' center interact with that of e_g of the M center it leads to ferromagnetic interactions, whereas interactions between $t_{2g}(\text{M}')\text{-}t_{2g}(\text{M})$ magnetic orbitals lead to antiferromagnetic interactions. In the case where both the t_{2g} and e_g orbitals present on M center both bear unpaired electrons, there is a coexistence of ferromagnetic and antiferromagnetic interactions with the t_{2g} magnetic orbitals of M' . The dominance of the antiferromagnetic interactions leads to a ferrimagnetic material.

The challenge in these molecular magnet studies is to build a magnetic system with an ordering temperature (T_c see equation below) close to or above room temperature. So far, the V/Cr (with $[\text{Cr}(\text{CN})_6]$) systems remain the only synthesized materials ordering ferrimagnetically and with a relatively high Curie temperature where values vary between 310 and 376 K.^{57,58,59,60,61}

$$kT_c = z|J|\sqrt{C_M C_{M'}} / N_A g^2 \beta^2$$

Equation: Neel's equation to fit the susceptibility of ferrimagnets in a range of temperatures close to the ordering temperature.⁶² z is the number of magnetic neighbors, $|J|$ is the absolute value of the exchange interaction, C_M and $C_{M'}$ are the Curie constants of M and M' respectively, N_A is the Avogadro constant, g is the Lande factor, β is the Bohr magneton.

1.3.2.2- Photomagnetic properties

In 1996, the group of Hashimoto reported⁶³ for the first time the photomagnetic properties of one of the Prussian Blue derivatives of formula $\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6]\cdot 6.9\text{H}_2\text{O}$. This was the beginning of a new research area that attracted considerable interest.^{64,65} The compound, the structure of which is mainly constituted of the $\text{Fe}^{\text{III}}\text{-CN-Co}^{\text{II}}$ pairs and a few $\text{Fe}^{\text{II}}\text{-CN-Co}^{\text{III}}$ pairs, also contains vacancies in the structure as can be seen from the non-stoichiometric formula. The compound has magnetic properties and the interactions between the metallic centers is antiferromagnetic with an ordering temperature of $T_c = 16$ K. Under irradiation with a red light (660 nm), an increase of the T_c of the compound up to 19 K was observed. The return to the initial state was possible by irradiating the compound with blue light (450 nm).

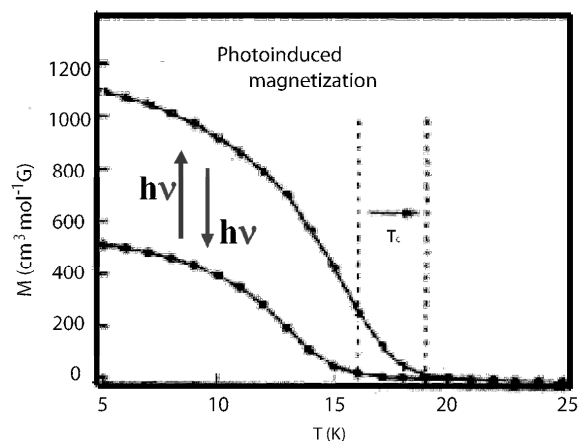


Figure 1.6: Photomagnetic effect of the compound $\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6] \cdot 6.9\text{H}_2\text{O}$ under irradiation. (Reproduced from reference 63).

The photomagnetic behavior of the compound, as represented in the figures 1.6 and 1.7, was attributed to an electron transfer from the Fe^{II} to Co^{III} with the cyanide behaving as electron transfer bridge and the process influenced by the cyano-alkali metal interactions.⁶⁶

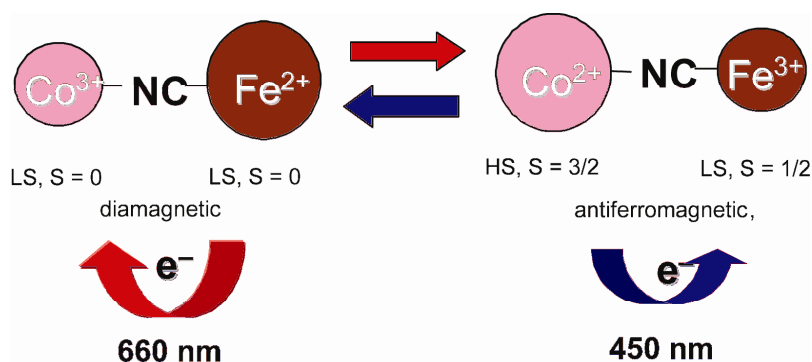


Figure 1.7: Photoinduced reversible electron transfer in the compound $\text{K}_{0.2}\text{Co}_{1.4}[\text{Fe}(\text{CN})_6] \cdot 6.9\text{H}_2\text{O}$.

In order to better understand the photomagnetic effect, several research groups synthesized various Co/Fe bimetallic compounds with different type or amount of the alkali cations $\text{A}_x\text{Co}_y[\text{Fe}(\text{CN})_6]_z \cdot n\text{H}_2\text{O}$ ($\text{A} = \text{K}^+, \text{Rb}^+, \text{Cs}^+$). The photomagnetic studies carried out on these compounds show a possible transition from either a diamagnetic or paramagnetic state to a ferromagnetic state or they can remain unaffected by irradiation, depending on the composition of the material.⁶⁷

Similar electron transfer properties were also reported for the complex $\text{Rb}_x\text{Mn}[\text{Fe}(\text{CN})_6]_y$, where under irradiation with light of 532 nm and 410 nm an electron transfer from Fe^{II} to Mn^{III} and back from Mn^{II} to Fe^{III} , respectively took place.⁶⁸ These results were reported soon after Ohkoshi et al. discovered a temperature induced charge transfer and magnetism with $\text{RbMn}[\text{Fe}(\text{CN})_6]$.⁶⁹ They could show that upon heating the

material, an abrupt increase of the magnetic susceptibility occurs at around 295 K and also abruptly decreases at around 220 K on cooling, in such a way that the cyclic measurement forms a hysteresis with a width of about 75 K. This was later assigned to the electron transfer from one metal to another⁷⁰ so that the system $\text{Fe}^{\text{III}}\text{-Mn}^{\text{II}}$ is predominant at low temperature while $\text{Fe}^{\text{II}}\text{-Mn}^{\text{III}}$ is formed at high temperature.

The photomagnetic behavior of the $\text{Co}/\text{Fe}(\text{CN})_6$ system happens to be favored by not only the presence of diamagnetic pairs $\text{Co}^{\text{III}}\text{-NC-Fe}^{\text{II}}$ in the structure but also by the presence of the amount of vacancies (Figure 1.8). The presence of these vacancies allows the expansion of the coordination sphere of metals during the electron transfer. The number of vacancies can be controlled by the type or the amount of the alkali metal used in the synthesis.⁷¹

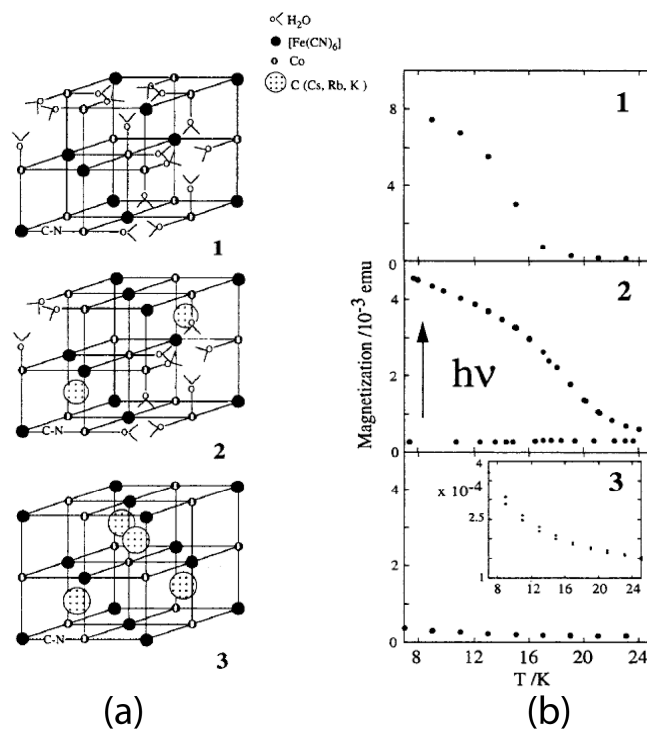


Figure 1.8: Representation of the structure (a) and photo-induced magnetization (b) of the Co/Fe system with different alkali cations. $\text{K}_{0.1}\text{Co}_4[\text{Fe}(\text{CN})_6]_{2.7} \cdot 18.4\text{H}_2\text{O}$ (1) contains 33% of $[\text{Fe}(\text{CN})_6]^{\text{IV}}$ vacancies, $\text{Rb}_{1.8}\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.3} \cdot 13\text{H}_2\text{O}$ (2) contains 17% of $[\text{Fe}(\text{CN})_6]^{\text{IV}}$ vacancies, $\text{Cs}_{3.9}\text{Co}_4[\text{Fe}(\text{CN})_6]_{3.9} \cdot 12.9\text{H}_2\text{O}$ (3) has no vacancies in the structure. (Reproduced with permission from reference 67).

In contrast to compound **2**, compounds **1** and **3** do not exhibit photomagnetic behavior. So the size of the alkali metal ion has to be optimum to control the number of the vacancies; and in this case rubidium is the optimum.

1.3.2.3- Other properties of the Prussian Blue Analogues.

Apart from the magnetic and photomagnetic properties that have been widely developed, other properties of PBAs have recently been considered.

1.3.2.3.1- Gas storage properties

Due to the porosity of some dehydrated PBAs, these compounds can allow for the insertion of other types of molecules such as gases or ions into their structure. Some of these materials have been reported for hydrogen storage.⁷² Yuan et al. have shown that the presence of the alkali metal ion K^+ in the porous structures could enhance the binding of H_2 .⁷³ The PBAs also have shown stability after adsorption of other gases^{74,75} such as CO_2 , N_2 , NO , SO_2 , H_2S and H_2O .

1.3.2.3.2- Electrical properties

The electrical conductivity of the Prussian blue analogues has been reported and therefore it is also described as an electroactive material.⁷⁶ In fact because of the presence of a gradient of reduced and oxidized Fe sites in the lattices of solvated Prussian blue, electron transport is expected between neighboring oxidized and reduced iron ions. Cyclic voltammetry showed that thin films of Prussian blue deposited on electrodes in aqueous^{77,78,79} and organic solvents⁸⁰ can be oxidized and reduced in two different ways according to: Fe^{III}/Fe^{II} to Fe^{III}/Fe^{III} and Fe^{III}/Fe^{II} to Fe^{II}/Fe^{II} conversions. Feldman and Murray⁸¹ described the effects of counteraction size, lattice oxidation state, and solvent population on electron conduction for a single, well-ordered Prussian blue film.

1.3.3- Some applications

Because of its magnetic and photomagnetic properties, the PBAs have the potential to be used in the development of new types of magneto-optical devices such as opto-magnetic memory devices which can be performed by selecting specific laser wavelengths. These materials can then transform light into mechanical energy.⁸²

In electrochemistry, the ability to modify the electrodes with a layer of PBA confers to these materials the possibility to be used as sensors for detection of certain compounds, such as ascorbic acid,⁸³ hydrazine,⁸⁴ hydroxylamine⁸⁵ or even hydrogen peroxide^{86,87} for which the detection limit varies between 2.10^{-7} M and 10.10^{-7} M. The electro-optical properties of PB are of interest as exemplified by Chen et al. recently in an electrochromic device (composed of working electrode, counter electrode and electrolyte) in which the

Prussian Blue compound is the anodic coloring material and shows good electrochemical stability.⁸⁸

1.4- Overview of the thesis

The goal of this thesis is to study the influence of the presence of a ligand L (with L being ethylenediamine or imidazole) on the properties of complexes of the type $[\text{Fe}(\text{CN})_5\text{L}]^{2-/3-}$. Also by using such complexes as building blocks in the synthesis of a new series of bimetallic systems of the type $\text{M}[\text{Fe}(\text{CN})_5\text{L}]$ (M = transition metal cation) the extent that the ligand L can tune the physical and chemical properties of these bimetallic systems can be determined by comparison with the general properties of PBAs. The basis of these studies is that PBAs of the type $\text{A}_x\text{M}_y[\text{Fe}(\text{CN})_6]_z$ (A = alkali metal cation) are mostly reported to crystallize into a three dimensional network and they are also called molecular-based magnets because they exhibit potentially useful electronic and magnetic behavior. This thesis is divided in two parts: Part 1 concerns the study of cyanometallate complexes and Part 2 focuses the study of the manganese(tmtacn) complexes

An overview of the cyanometallate complexes is provided in this Chapter.

In Chapter 2 several substituted pentacyano(L)ferrate compounds of the type $\text{Na}_3[\text{Fe}^{\text{II}}(\text{CN})_5\text{en}] \cdot 5\text{H}_2\text{O}$ and $(\text{PPh}_4)_2[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}] \cdot 2\text{H}_2\text{O}$ (with en = ethylenediamine, PPh_4^+ = tetraphenylphosphonium cation and im = imidazole) are examined. The former is a yellow complex isolated from the reaction of sodium nitroprusside with an excess of the ethylenediamine, the latter is red brown complex obtained from air oxidation of the former complex in the presence of a tetraphenylphosphonium chloride salt. Although both ligands (en and im) contain two nitrogen atoms, the structure of both complexes shows monodentate behavior of these ligands towards the iron ion. Spectroscopic studies reveal the low-spin Fe(II) (former) and the low-spin Fe(III) (latter) character of the complexes.

Chapter 3 extends the study of the $(\text{PPh}_4)_2[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}] \cdot 2\text{H}_2\text{O}$ complex especially in its use as building block in the synthesis of a new series of bimetallic complexes of the type $\text{M}[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}] \cdot x\text{H}_2\text{O}$ (where M = Mn^{2+} , Co^{2+} and Zn^{2+}) and $\text{Mn}(\text{byp})[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}]$. The structural characterization of these complexes using single crystal X-ray diffraction confirm the bridging character of the cyano ligands; it is revealed that compared to other Prussian Blue Analogues, which mostly crystallize in three dimensional systems, these complexes adopt a two-dimensional network. These planar systems are such that the cyano

ligand in the *trans* position of $[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}]$ remains terminal and does not show bridging character. Quantitative analysis using SQUID magnetometry shows the amelioration of the magnetic property of the bimetallic systems especially the Co/Fe due to the presence of the imidazole ligand.

Chapter 4 is devoted to the mechanistic study of the formation of the $(\text{PPh}_4)_2[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}] \cdot 2\text{H}_2\text{O}$ complex from $\text{Na}_3[\text{Fe}^{\text{II}}(\text{CN})_5\text{en}] \cdot 5\text{H}_2\text{O}$. Several spectroscopic methods (UV-vis, Raman) are used in kinetic studies to identify the origin of the extra carbon reacting with the ethylenediamine to form the imidazole ligand in the product complex.

Chapter 5 describes the influence of the substituents (R group) on the general properties of manganese complexes of the type $[\text{Mn}^{\text{III}}_2(\mu\text{-O})(\mu\text{-R-CO}_2)_2(\text{tmtacn})_2]$ (tmtacn = N,N',N'',-trimethyl-1,4,7-triazacyclononane). The goal of this chapter is to ascertain if electrochemical and spectroscopic data can give predictive insight into the selectivity and activity of the catalysts in the oxidation of alkenes.

Chapter 6 describes the various analytical methods used in the analysis of all the compounds represented in this thesis.

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