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## Magnetic and spectroscopic studies of iron and manganese complexes

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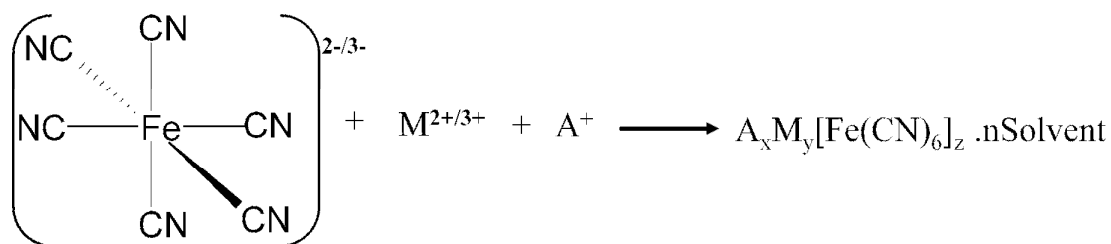
## SUMMARY

The chemistry of Prussian Blue Analogs (PBAs) has been explored extensively, and has led to a wide range of applications due to their peculiar properties. The most representative family of PBAs are those of the type  $A_xM_y[M'(CN)_6]_z \cdot nH_2O$ ; an inorganic polymer is formed in these systems with the cyano acting as a bridging ligand between the two metal ions ( $M^{n+}$  and  $M'^{p+}$ ) resulting in a three dimensional (3D) structure. The structure typically contains defects, which are useful since they allow for properties to be tuned. The presence of two metal centers in the molecule, which can interact magnetically with each other, gives to the system the name *molecular-based magnet*. Under irradiation, the cyano ligands can facilitate electron transfer between both metal centers when they are in different oxidation states. In PBAs, the presence of defects in the structure is common and can be an advantage; however, control of the number of defects is still non-trivial.

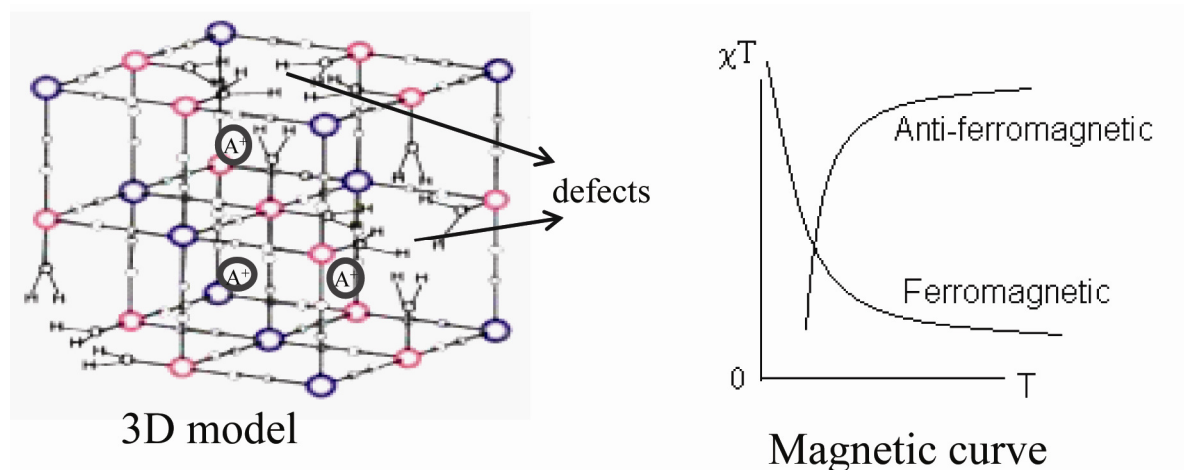
This thesis focusses on the synthesis of a new series of bimetallic compounds of the type  $M[M'(CN)_5L] \cdot n(\text{solvent})$  from substituted complexes of the type  $[Fe(CN)_5L]^{2+/3+}$ . The properties of these mononuclear cyanides, how they can influence the stoichiometry and the structure of bimetallic systems and to what extent their use as building blocks can tune the properties of new bimetallic complexes were investigated.

The work presented in this thesis is divided into two main topics. The first part presented in chapters 2, 3 and 4 describe the formation and the properties of metal cyano complexes. The second part described in chapter 5, deals with study of the relation between electrochemical and spectroscopic data and the selectivity and activity of a series of catalysts made from substituted benzoic acids with a manganese-(tmtacn) complex (tmtacn = N,N',N'',-trimethyl-1,4,7-triazacyclononane).

Chapter 1 of this thesis presents an overview of the studies of cyanide metallate complexes and a discussion of the diverse fields of application. The formation of 3D networks of Prussian Blue Analogs (PBAs) from the mononuclear hexacyanoferrate complex is discussed.

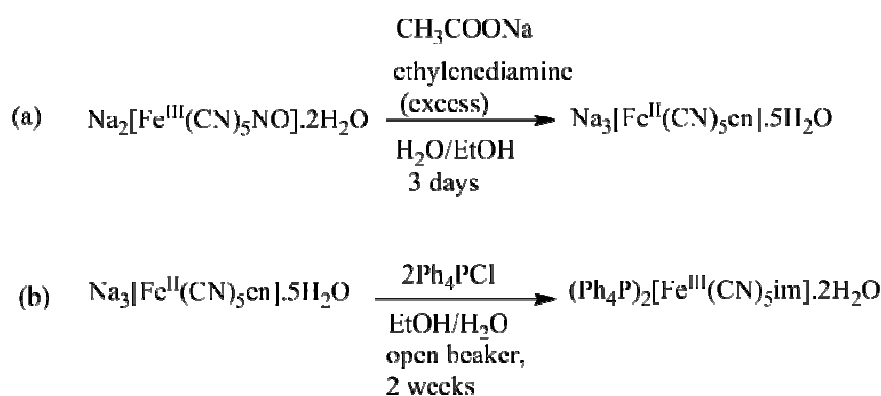


**Figure 1:** General synthesis procedure for preparation of PBAs.



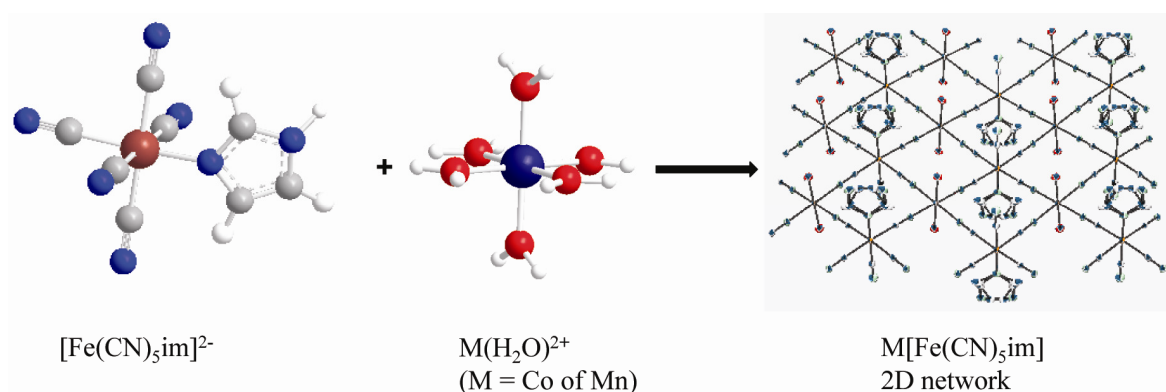
**Figure 2:** 3D representation of a PBA with defects and magnetic susceptibility curves expected for ferromagnetic and anti-ferromagnetic behavior.

In Chapter 2, we described the synthesis of two mononuclear cyanide complexes  $\text{Na}_3[\text{Fe}^{\text{II}}(\text{CN})_5\text{en}] \cdot 5\text{H}_2\text{O}$  (en = ethylenediamine) (**1**) and  $(\text{Ph}_4\text{P})_2[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}] \cdot 2\text{H}_2\text{O}$  (im = imidazole) (**2**) is described. Complex **1** is obtained from the reaction of sodium nitroprusside ( $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ ) with an excess of ethylenediamine whereas **2** is isolated from an aqueous solution of **1** with  $\text{Ph}_4\text{P}\text{Cl}$ . The characterization of these compounds reveals that both complexes have an octahedral environment with the metal center coordinated to five cyano ligands and one of the nitrogens of the ethylenediamine or imidazole ligand. FT-IR and Raman spectroscopy show that the Fe(II) ion in **1** is divalent whereas it is trivalent in **2**. Complex **1** does not show any EPR or MCD signal confirming that the metal center is diamagnetic and therefore low spin. However, magnetic studies on complex **2** reveal the low spin state of the Fe(III) ion and the paramagnetic properties of the complex.



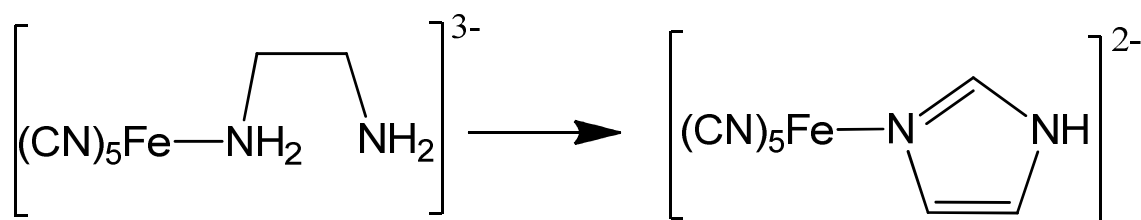
**Scheme 1:** Synthesis of **1** (a) and **2** (b).

Chapter 3 addresses the use of  $(\text{Ph}_4\text{P})_2[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}] \cdot 2\text{H}_2\text{O}$  as a building block in the synthesis of a new series of bimetallic systems of the type  $\text{M}[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}] \cdot n(\text{solvent})$  (where M is transition metal ions  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$  or  $\text{Zn}^{2+}$ ). From X-ray data,  $[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}]^{2+}$  binds to the other metal ions through its four equatorial cyano ligands, with the axial cyano ligand is non-bridging. This bonding leads to the formation of a 2D network. The coordination of the imidazole to the Fe(III) ion results in a significant *trans* effect on the axial cyano ligand, which reduces its ability to bridge a second metal ion. However the exception is for the system formed with zinc ions, which shows a 3D network and in which all the five cyano ligands are involved in the bridging between the two metal ions. From SQUID measurements, it was found that although initially the mononuclear complexes of  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$  and  $\text{Mn}^{2+}$  are paramagnetic, when forming a bimetallic system, they interact magnetically to realize either ferromagnetic behavior (in case of  $\text{Fe}^{3+}/\text{Co}^{2+}$  and  $\text{Fe}^{3+}/\text{Mn}^{2+}$ ) or weak antiferromagnetic behavior (the case of  $\text{Fe}^{3+}/\text{Mn}^{2+}$ (bypiridine)). The system formed with zinc ( $\text{Fe}^{3+}/\text{Zn}^{2+}$ ) does not show intermetallic interaction since  $\text{Zn}^{2+}$  is diamagnetic. The system  $\text{Co}[\text{Fe}^{\text{III}}(\text{CN})_5\text{im}]$  presents an improved Curie temperature ( $T_c = 25$  K) compared to that of  $\text{Co}_x[\text{Fe}^{\text{III}}(\text{CN})_6]_y$  (with a  $T_c = 16$  K). The use of substituted imidazoles offers a considerable handle to tuning the solid state properties. The improvement of the Curie temperature is advantageous in the design of new magnetic devices. This compound could eventually exhibit a photo-induced enhancement of the magnetization at low temperature with an increase of the Curie temperature, which will be higher than that of the  $\text{Co}_x[\text{Fe}^{\text{III}}(\text{CN})_6]_y$  (with a  $T_c = 22$  K). Also the closer the Curie temperature is to room temperature, the better magneto-optical signal the compound can exhibit.



**Figure 3:** Formation of a 2D network in the bimetallic system  $\text{M}[\text{Fe}(\text{CN})_5\text{im}]$

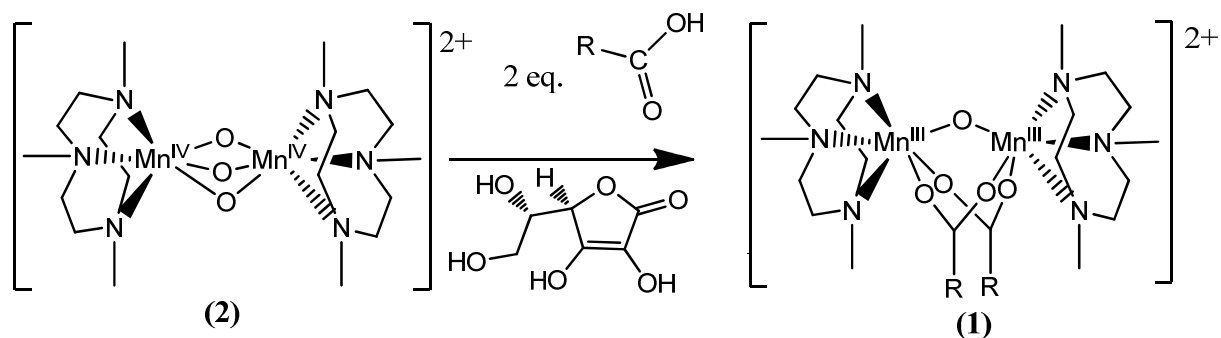
Chapter 4 focuses on a mechanistic study of the formation of the imidazole complex from the ethylenediamine complex including the determination of the source of the extra carbon to form the imidazole ring (scheme 2). It was found that the only possible sources of the extra carbon atom to form the imidazole are the ethylenediamine and from the cyano ligands. The results obtained from labeling studies carried out with  $\text{K}^{13}\text{CN}$  as well as from the various spectroscopic analyses revealed that the ethylenediamine is the carbon donor for the formation of imidazole. The yield of the reaction (60%) leads to the assumption that three equivalents of ethylenediamine complex react with each other to give two equivalents of imidazole complex. Therefore, a better understanding of this mechanism holds implications for C-C (of ethylenediamine) bond cleavage.



**Scheme 2:** Formation of imidazole complex from ethylenediamine complex.

In chapter 5, the influence of substituted R-carboxylato ligands (R = alkyl, alkylhalide or (substituted) phenyl) on the general properties of manganese complexes of the type  $[\text{Mn}^{\text{III}}_2(\mu\text{-O})(\mu\text{-R-CO}_2)_2(\text{tmtacn})_2]^{2+}$  (tmtacn = N,N',N'',-trimethyl-1,4,7-triazacyclononane) is discussed. The aim of the chapter was to ascertain if electrochemical and spectroscopic data can give predictive insight into the selectivity and activity of the catalysts in the oxidation of alkenes. The results obtained indicate that, although control of the selectivity and/or activity of the catalyst is achieved by variation of the substitution of benzoato based

catalysts, electrochemical and spectroscopic properties show no relationship to catalytic properties.



**Scheme 3:** Synthesis reaction of the substituted  $[\text{Mn}_2(\mu\text{-O})(\mu\text{-RCO}_2)_2(\text{tmtacn})_2]^{2+}$ .

In chapter 6, a brief description of the analytical techniques used to characterize the samples reported in this thesis is given.

