Exploring coordination chemistry and reactivity of formazanate ligands
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**English Summary**

Redox-active ligands have been the focus of intensive investigation in the last decades due to their ability to act as electron reservoirs during redox reactions without involving the metal center. Many metals are not suitable for two electron reactions because of the presence of only one stable oxidation state, or two states that differ by only a single electron. Thus, scarce and expensive metals are employed for many of the catalytic reactions. Redox-active ligands have the potential to change the concept of catalysis to ligand-based reactions where the ligand is the site accepting or donating electrons and the metal is a mere spectator, being able, in this way, to use a much wider variety of metals, including cheap, non-noble elements.

Throughout this thesis we employ a redox-active ligand, formazanate, and we combine it with different metal centers (Na, K, Mg, Ca, Zn and Fe). Synthesis, characterization and investigation of the different properties and applications with the different combinations of formazanates-metal combinations are investigated through the different chapters (2 to 7) with the first chapter serving as an overview of naturally occurring and bio-inspired redox-active ligands. The results presented in this thesis provides a better insight of the behavior of this ligand when varying the nature of the metal center and provide a series of new applications of the formazanate ligand framework.

In *Chapter 1*, an introduction into ‘redox-active ligands’ is provided. The requirements of a ligand to potentially act as a ‘redox-active’ is described, and two examples from nature that make use of these ligands are given by cytochrome P-450 and galactose oxidase enzymes. Due to the importance of these classes of ligands, in the last decades many efforts have been done to emulate nature. Thus, bio-inspired redox-active ligands such as catecholate and its derivatives have gained attention. In addition, the chapter presents a brief comparison between the closely structurally related β-diketiminate and formazanate ligands, with a focus on their differences in redox-reactivity.

In *Chapter 2*, the synthesis of various formazanate alkali metal salts (ML) is presented by modifying the substituents of the formazanate ligand (L) and/or the metal center (M = Na or K). The crystal structures show high flexibility of the formazanate backbone leading to
various coordination modes as a result of the binding of internal (1-K and 2-Na) and/or terminal (3-Na) nitrogen atoms leading to 4- and 5-membered chelate structures, respectively. Also, solid-state studies reveal the influence of the 4 nitrogens present in the formazanate framework by intramolecular interactions for the different complexes, leading to aggregates that range from dimeric (K[PhNNC(p-tol)NNPh]-2THF 1-K) to hexameric (Na[PhNNC(t-Bu)NNPh] 3-Na) and polymeric (Na[MesNNC(CN)NNMes]-2THF 2-Na) (Figure 1).

Figure 1. X-ray structure of the different alkali metal salts presented in Chapter 2, showing the different aggregation in the solid state (1-K top left, 2-Na top center and top right, 3-Na bottom left and 1-NBu4 bottom right). Structures showing 50% probability ellipsoids with hydrogen atoms omitted for clarity.

1H NMR spectroscopy studies show sharp peaks for all the compounds suggesting monomeric structures in solution-state for all the complexes except for 1-K. For this last compound, variable-temperature (-25 °C to 80 °C) and low temperature EXSY (-25 °C) indicate retention of the dimeric structure in solution-state, even in THF. In the absence of coordinating metal center the formazanate show a 'linear' conformation with no interaction with the cation employed (NBu4+, Figure 1).
The synthesis of the alkali metal salts presented on this chapter opens up a new synthetic route for formazanate complexes via metathesis, as discussed in more detail in Chapter 3 and 7.

In Chapter 3, we discuss the synthesis of alkaline earth formazanate complexes employing magnesium and calcium (ML₂(THF)ₙ, M = Mg, Ca). On the one hand, magnesium complexes were synthesized by deprotonation of the corresponding free formazans (LH) with MgBu₂, resulting in the pseudo-tetrahedral coordination environment for MgL₂ complexes in the absence of THF (1,3,4,6,8,9-Mg). Due to the Lewis acidity of magnesium, the mono-THF adducts (MgL₂(THF)) could be synthesized in the presence of THF (1,3,4,6-MgTHF). X-ray crystal structures show binding of the formazanate to the metal center through the two terminal nitrogens atoms, leading in all the cases to 6-membered chelate rings, with the exception of 9-Mg, where two binding modes were found, 6- and 5-membered chelate ring (Figure 2). These two isomers of 9-Mg are also present in solution state in a dynamic equilibrium indicated by two sets of resonances present. When fluorinated aromatic N-substituents are introduced, the compounds show additional weak F⁻·Mg interactions, that are broken in the presence of better Lewis bases such as THF (Figure 2).

On the other hand, the calcium analogues could be synthesized via two different routes: (I) direct synthesis from the formazan ligand and Ca(NTMS)₂(THF)₂ or (II) through metathesis of CaI₂ with the alkali metal salts discussed in Chapter 2. In all the cases, these calcium complexes show only the 6-membered chelate ring isomer in solution and solid state.
Depending on the steric demands of the ligand substituents, complexes with different coordination numbers are obtained that differ in the number of THF molecules that are bound. Trends in the UV-Vis absorption spectra and cyclic voltammetry data are discussed and compared to the Zn analogues previously reported.

In Chapter 4, a straightforward synthesis of tetrazepines (4.1/4.2) and arylazoindazoles (4.3/4.4) by Nucleophilic Aromatic Substitution is presented that takes place via cyclization of formazanate anions that have C₆F₅-substituents. Some of the remaining aromatic C-F bonds are susceptible to further substitution, as shown by the preparation of single (4.1OMe, 4.3SCH₂) and double (4.1OMe, 4.2OMe) Nucleophilic Aromatic Substitution products. (Figure 3). All the compounds were purified by simple filtration (4.1, 4.2, 4.1OMe, 4.2OMe), crystallization (4.3, 4.4, 4.3OMe) or extraction (4.3SCH₂) and characterized in detail. Homo- and heteronuclear NMR experiments (¹H,¹⁹F: NOE and HOESY) were used to unequivocally establish the position of the substituents(s) on the functionalized arylazoindazole and tetrazepines. Kinetic studies were performed to probe some of the mechanistic details and provide a rationale for product distributions for unsymmetrical substrates.

The cyclic voltammetry of tetrazepines shows two quasi-reversible redox couples (e.g., for 4.1: -1.42 V and -2.25 V versus Fe⁺). The first electron process would generate the radical anion in which the unpaired electron is assumed to be delocalized over the four nitrogens similarly to verdazyl radicals. Cyclic voltammetry studies were also performed for the arylazoindazole 4.3. However, only one quasi-reversible redox couple is present, which occurs at more negative potential than for the tetrazepines (-1.84 V versus Fe⁺).

In Chapter 5, we discuss the photochemistry of the arylazoindazole compounds described in the previous chapter. UV-Vis spectroscopy of pure E arylazoindazoles in toluene show a broad absorption around 350 nm and a weaker, in same cases, very broad around 450
nm which are attributed to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively. In all the cases, irradiation at $\lambda_{irr} = 365$ nm leads to $E\rightarrow Z$ isomerization with photostationary states that range from 75% to 92% of $Z$-isomer. Similarly, the regeneration of the $E$ isomer was achieved by irradiation at $\lambda_{irr} = 420$ nm with lower PSS (46-70%) due to some overlapping of the absorption bands of both isomers. In addition to the moderate to high photoconversion of all the arylazoindazoles studied, they also possess long thermal half-lives ($t_{1/2} = 1.6$ to 7.7 days) and good fatigue resistance with no photobleaching taking place, even upon irradiation over 20 days. Changes in the polarity of the media by going from toluene to DMSO did not have influence in the photochemistry performance. Also substitution of F for O- or S-alkyl groups (4.3, 4.3OMe and 4.3SC8H17, respectively) did not affect the photochemical and thermal switching behaviour.

Transition state calculations for 4.3, 4.4 and 4.3OMe indicate that thermal $Z\rightarrow E$ isomerization follows the rotational pathway as this presents the lowest barrier.

In Chapter 6, several formazanate complexes were synthesized, characterized and tested towards conversion of lactide. These complexes can be gathered in three kind of catalysts: (I) mono(formazanate) zinc methyl (LZnMe), (II) bis(formazanate) (ML2, M = Zn, Mg, Ca) and (III) mono(formazanate) alkoxy complexes (LMOR, M = Zn, Mg). This last group, show in all the cases dimeric structures in solid state (Figure 4). However, DOSY NMR experiments reveal dimeric or monomeric structures depending on the steric effects of the alkoxide. All the complexes show activity in the conversion of lactide, achieving the highest rate when 1-MgOC(CH3Ph2) is employed, by converting 20 equivalents of lactide in less than an hour. Although more studies are needed to clarify the precise nature of the initiating groups, a trend in conversion is followed by going to a larger, more Lewis acidic metal center (Ca > Mg > Zn) and by the presence of better nucleophiles as initiator groups (LMOR > ML2 > LMMe).
Figure 4. Molecular structures of 1-ZnOR, 5-ZnOiPr showing 50% probability ellipsoids. The hydrogen atoms in all structures and the solvate molecules in 1-ZnO′Bu (pentane) and 1-ZnOPh (toluene) are omitted for clarity.

Cyclic voltammetry studies were performed for some representative complexes (1-ZnMe, 1- and 5-ZnOiPr). The monomeric zinc methyl complex shows two quasi-reversible redox couples (-1.63 V and -2.39 V versus FeO+/+) corresponding to the one- and two-electron processes which generate the radical anion \([\text{LZnMe}]^-\) and the dianionic species \([\text{LZnMe}]^{2-}\), respectively. The dimeric zinc alkoxide 1-ZnO′Pr show three redox-events. The first two reductions are close to each other (-1.51 V and -1.73 V vs. FeO+/+), suggesting the sequential single-electron reduction for each formazanate in the dimer leading to \([\text{LL′Zn}_2(\mu-\text{OiPr})_2]^{+}\) and \([\text{L′L′Zn}_2(\mu-\text{OiPr})_2]^{2-}\), respectively (L = formazanate anion, and L’ = formazanate radical dianion). Lastly, the monomer 5-ZnO′Pr shows a complex voltammogram, likely due to chemical reactions taking place after reduction.

In Chapter 7, the synthesis and detailed characterization of a bis(formazanate) iron(II) (1-Fe) and its singly reduced complex ([1-Fe][NBu₄]) are described. Variable temperature NMR, Mössbauer, SQUID, variable temperature UV-Vis, Xray, DFT, CV and Differential scanning calorimetry have been combined to be able to elucidate the unusual magnetic properties of both formazanate complexes. The \(\pi\)-acceptor ability of the formazanate leads \(\pi\)-backdonation, which stabilizes one of the d-orbitals that is normally anti-bonding in a...
tetrahedral complex and leads to an unusual ‘inverted’ ligand field. As a consequence, 1-Fe and [1-Fe][NBu₄] exhibit unique properties (Figure 5). 1-Fe is presented in this chapter as the first example of spin-crossover in a pseudo-tetrahedral complex. In solution state at low temperature the compound is shown to possess a diamagnetic (S = 0) ground state, but spin-crossover to a S = 2 spin state occurs at higher temperature (T_{1/2} = 345 K). This thermal switching between S = 0 and S = 2 is reversible in the solution state. In solid state this change in transition does not occur till 450 K, temperature that lead to a change in the unit cell and an increase in 7% volume.

Similarly, for the 1-electron reduced analogue the π-acceptor properties of the formazanate also leads to a low-spin center of the corresponding anion [1-Fe][NBu₄], which is shown to contain a rare S = ½ Fe(I) center. Therefore, both complexes behave as π-acceptors rather than ‘redox-active’ ligands.

Figure 5. Stabilization of the dyz orbital of the formazanate ligand due to their π-acceptor character.