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THE OPTICAL AND MAGNETIC PROPERTIES OF REDOX-ACTIVE D-BLOCK METAL COMPLEXES WITH NON-INNOCENT LIGANDS

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ABSTRACT

Redox-active metal organic complexes with ‘non-innocent’ ligands are promising candidates when it comes to developing novel homogenous catalysts. The related complexes have gained interest since they could be utilized as affordable base-metal containing compounds instead of expensive and scarce noble metal containing complexes. The complexes with non-innocent ligands undergo readily one- or multielectron oxidation/reduction processes, which are vital in catalytic processes. Therefore, the complexes have been studied for biomimetic model compounds for metalloenzymes.

These redox-active complexes have low-lying, intramolecular charge transfer processes that enable the compounds to absorb strongly electromagnetic radiation at low frequency range, namely, in the near-infrared range. In addition, the complexes possess interesting magnetic properties which are potentially influenced by photon excitation. Some of the redox-active complexes bear unpaired spins on the orbitals of the organic ligands. Redox-active complexes, in some cases, do exhibit bistability and are known to go through valence tautomerization process, where the sum of the electrons within the complex remains, while their locations and orientations vary. This may result in differing spin states within the complex and thus differing physical (optical and magnetic) properties between the tautomers.

These features are the key in order to use these complexes in various sensing applications or in molecular memory. Because of their intense absorptions, the redox-active complexes have also been considered as dye sensitizers in a titanium dioxide-based dye sensitized solar cells and other photovoltaic applications. The present thesis exhibits the synthesis, characterization and the redox-active, optical and magnetic properties of first-row d-block metal complexes with non-innocent ligands.

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TIIVISTELMÄ

Hapetus-pelkistysaktiiviset metalliorganiset kompleksit, joilla on ns. ”arveluttavia” (*engl. non-innocent*) ligandeja, ovat lupaavia ehdokkaita uusien, substraatin kanssa samassa faasissa reagoivien, katalyyttien kehittämiseksi. Kyseiset kompleksit ovat saaneet huomiota osakseen, sillä niitä voidaan hyödyntää edullisina, perusmetalleja sisältävinä yhdisteinä kalliiden sekä harvinaisten, jalometalleja sisältävien yhdisteiden sijaan. Ne kompleksit, joilla on ”arveluttavia” ligandeja, käyvät vaivattomasti läpi yhden tai useamman elektronin hapetus-pelkistysreaktioita, jotka ovat olennaisia katalyyttisissä prosesseissa. Siksi näitä yhdisteitä on tutkittu myös siirtymämetalleja sisältävien entsyymien aktiivisten keskusten toiminnan jäljittelemisessä.

Näillä hapetus-pelkistysreaktioihin taipuvaisilla yhdisteillä on myös matalaenergisiä molekyylinsisäisiä varauksensiirtoprosesseja, jotka mahdollistavat yhdisteiden voimakkaan sähkömagneettisen säteilyn absorptioon matalalla taajuusalueella, nimittäin lähi-infrapuna-alueella. Lisäksi kompleksit omaavat kiinnostavia magneettisia ominaisuuksia, joihin mahdollisesti voidaan vaikuttaa virittämällä yhdisteitä valolla. Joillakin hapetus-pelkistysreaktioihin taipuvaisilla yhdisteillä on parittomia elektroneja orgaanisten ligandiensa orbitaaleilla. Hapetus-pelkistysreaktioihin taipuvaisten yhdisteiden tunnetaan joissakin tapauksissa myös osoittavan useita pysyviä rakenteita, eri olosuhteissa, ja siten käyvän läpi molekyylin sisäistä hapetuslukujen tautomerisaatiota, jossa elektronien summa pysyy samana, mutta niiden sijainti sekä elektronien spinien suuntautuminen muuttuvat. Tautomeerien välillä voi olla eriäviä fysikaalisia (optisia ja magneettisia) ominaisuuksia, jotka johtuvat eriävistä spintiloista.

Nämä piirteet ovat erittäin tärkeitä, jotta näitä yhdisteitä voitaisiin hyödyntää erilaisissa ilmaisimissa tai molekyylikokoluokan muistissa. Voimakkaiden absorptioidensa vuoksi näitä yhdisteitä on myös harkittu käytettävän väriaineina titaanidioksidipohjaisessa väriaineherkistetyssä aurinkokennossa ja muissa valosähköiseen ilmiöön pohjautuvissa sovelluksissa. Tämä väitöskirja käsittelee ensimmäisen rivin d-lohkon, ”arveluttavien” ligandien omaavien, metallikompleksien synteesejä, karakterisointeja sekä niiden hapetus-pelkistysprosessien, sekä optisten että magneettisten ominaisuuksien tutkimista.

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Abbreviations

3,5-dtbc	3,5-di- <i>tert</i> -butylcatechol
Cp*	pentamethyl cyclopentadiene
CV	cyclic voltammetry
cyclam	1,4,8,11-tetraazacyclotetradecane
DFT	density functional theory
DSC	differential scanning calorimetry
DSSC	dye sensitized solar cell
EPR	electron paramagnetic resonance
FT	fourier transform
HOMO	highest occupied molecular orbital
HS	high-spin
IR	infrared
LLCT	ligand-to-ligand charge transfer
LMCT	ligand-to-metal charge transfer
LS	low-spin
LUMO	lowest unoccupied molecular orbital
MLCT	metal-to-ligand charge transfer
NIL	non-innocent ligand
NIR	near infrared
pap	2-phenylazopyridine
PMMA	poly(methyl methacrylate)
SQUID	superconducting quantum interference device
TGA	thermogravimetric analysis
tppz	2,3,5,6-tetrakis(2-pyridyl)pyrazine
tren	tris(2-aminoethyl)amine
vis	visible light
VT	valence tautomerization
UV	ultra-violet

List of Original Publications

This dissertation is based on the following original publications, which are referred to in the text by their Roman numerals:

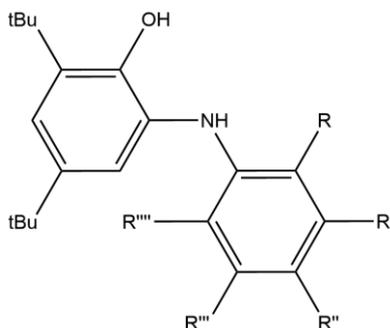
- I Salojärvi, E., Peuronen A., Huhtinen, H., Vlasenko, L. S., Halme, J., Mäkinen, P., Lastusaari, M., Lehtonen, A. NIR-absorbing Transition Metal Complexes with Redox-Active Ligands. *Inorganic Chemistry Communications*, 2020; 112: 107711-107714.
- II Salojärvi, E., Peuronen A., Lahtinen, M., Huhtinen, H., Vlasenko, L. S., Lastusaari, M., Lehtonen, A. Series of Near-IR-Absorbing Transition Metal Complexes with Redox Active Ligands. *Molecules*, 2020; 25: 2531-2547.
- III Salojärvi, E., Peuronen A., Moilanen, J., Huhtinen, H., Lindén, J., Mansikkamäki, A., Lastusaari, M., Lehtonen, A. Iron Complex of a Non-Innocent Ligand with a Controlled Intra-Ligand Cyclisation and a Rare Example of a Partial Thermally Induced Magnetic Alteration of an Iron Complex. (manuscript)

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1 Literature Review

1.1 Introduction

The term 'non-innocence' was coined in chemistry by Jørgensen in 1966.¹ In coordination chemistry, 'non-innocence' refers to state the ambiguousness of the actual oxidation states of the central atom(s) and the coordinated ligands. Many, even the simplest molecules may have various oxidation states and thus act as a non-innocent ligand (NIL), such as NO and O₂. For example, dioxygen can coordinate as peroxide (O₂²⁻) or as superoxide (O₂⁻).² In theory, almost any ligand can coordinate to the metal ion in anionic or radical form and hence 'non-innocently'. Although one could draw even the most exotic resonance structures for a metal organic complex, in practice, however, it is quite rare to have compounds that are truly isolable in all theoretical resonance structures.



Scheme 1 N-arylamino phenolato proligand derivatives that are discussed in this thesis.

Not long after Jørgensen's coinage, the first N-arylamino phenol proligand and its metal complex was reported.^{3,4} The 2,4-di-*tert*-butyl-6-(phenylamino)phenol and its derivatives are a subject of interest for their stability and simple synthesis. Commonly, the proligand (Scheme 1) is synthesized by a condensation reaction between 3,5-di-*tert*-butylcatechol (3,5-dtbc) and a primary, aromatic amine. The proligand is then extracted and subsequently used in complex syntheses but there are examples where the N-arylamino phenolato ligand is directly formed during the complexation.^{5,6} In addition, the metal complexes of N-arylamino phenol usually

exhibit strong NIR absorptions almost regardless of the metal center. This feature raises interest towards these compounds because of their potential use in molecular sensing,⁷ recording,⁸ medical imaging⁹ and camouflaging.¹⁰

Metal organic complexes with NILs have been studied for biomimetic metalloenzyme model compounds, mainly as electron reservoirs in the catalytic cycle. The redox activity of these complexes permits the redox processes and thus bond breaking and forming between the substrate and the central metal, which is essential for the catalytic processes. The complexes may also contain electrons with unpaired spins on the orbitals of the organic ligands, which then results in rather elusive oxidation states for the ligands as well for the central metal ions. The unpaired spins, too, cause the complexes to have intriguing magnetic properties due to the intramolecular (anti)ferromagnetic coupling.

1.1.1 Magnetic Properties of Coordination Compounds

Most of the d-block metals, apart from the group 12 metals, have partially filled d-orbitals. These metals are called ‘transition metals’. Transition metal compounds have five valence d-orbitals. Within the orbitals may reside *electrons*. Electron is an elementary particle that has a negative charge and it has angular momentum of $S = \pm 1/2$ (*spin*). According to the Pauli Exclusion Principle,¹¹ two or more electrons cannot occupy the same quantum state in one system at the same time. Thus, each orbital can host maximum of two electrons, on the condition that they have oppositely directed spins.

If there is an odd number of electrons on the valence orbitals of the metal, or if an even number of electrons have arranged as such that there is a non-zero net spin moment on the atom, then the metal is *paramagnetic*. Atoms, ions and molecules with zero net spin moment are called *diamagnetic*. Paramagnetic compounds are attracted by external magnetic field and diamagnetic repelled by external magnetic field. If spin moments are aligned parallel in a compound or a lattice, then they are *ferromagnetically coupled*. Ferromagnetic coupling thus increases the net magnetic moment in a paramagnetic compound. *Anti-ferromagnetic coupling*, on the other hand, decreases the net magnetic moment in a compound when the opposing spin moments cancel each other out. Hence, a compound with multiple radical moieties can be diamagnetic if the spin moments sum up to zero.

Transition metal ions, even though on a one formal oxidation state, may exhibit different spin states. For example, Fe^{2+} has six electrons on its valence d-orbitals and can have 0, 2 or 4 singly occupied d-orbitals. These spin states are referred as low-spin (LS), intermediate-spin and high-spin (HS), respectively. According to the Hund’s Rule, all the subshells of an orbital are singly occupied with parallel spins before any subshell is occupied by two electrons. However, the different spin states

are possible due to ligand orbital splitting. Several factors have an impact on this splitting: the natures of the metal ion and ligands, the oxidation state of the metal, the coordination geometry of the complex molecule and the ordering of the ligand around the central metal ion. Figure 1 illustrates the fact that the energy difference between the two degenerate states in the octahedral Fe^{2+} complexes' d-orbitals effects on the 'building up' of the orbitals. Formerly mentioned intermediate-spin square-planar and square-pyramidal Fe^{2+} complexes are known¹²⁻¹⁴ but are relatively uncommon when compared to octahedral LS and HS Fe^{2+} complexes.

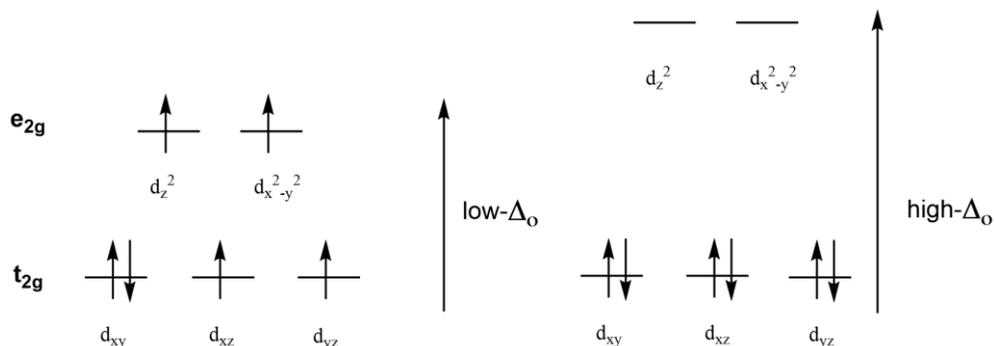


Figure 1 The high-spin ($S = 2$) (left) and the low-spin ($S = 0$) (right) d-orbital energy level diagrams of an octahedral Fe^{2+} complex.

In practice, the biggest difference in magnetic properties between complexes is if the studied complex is diamagnetic or not. If it is, then the complex can be structurally studied in solution with ^1H and ^{13}C -NMR (nuclear magnetic resonance) spectroscopy and thus obtain information on the organic ligands. In theory, even the diamagnetic metal center may be directly studied with NMR spectroscopy but the results are difficult to compare with rather scarce literature and thus provide little information. If the complex is paramagnetic, then the NMR spectroscopy probably does not provide much structural information due to signal broadening. The EPR (electron paramagnetic resonance) spectroscopy and the SQUID (superconducting quantum interference device) measurements would provide information about the compounds' magnetic properties, such as the net magnetic moment of the complex (in the function of temperature), and the nature of the paramagnetic species *i.e.* if it is metal-centered or an organic radical and whether the compounds magnetic properties alter under variable temperature or magnetic field. Both of the methods provide virtually zero information on diamagnetic compounds but also some paramagnetic moieties, such as HS Ni^{2+} ($S = 1$), can be EPR silent and thus give no detectable signal.

Also some complexes exhibit multiple stable spin- or valence states under varying conditions. These features are referred as *spin crossover* and *valence tautomerism* (VT). Spin crossover behavior means that some external stimulus, such as temperature, causes the studied complex to undergo a reversible, structural reformation that causes the central metal atom to change its spin state from LS to HS. For example, some Fe²⁺ complexes¹⁵ behave in this way. VT is a similar process but it requires the change in formal oxidation states of the compound's atoms. This means that the central metal ion usually needs to have a stable redox pair and the organic ligands should be redox-active in order to the VT process to take place. These features are of interest because they may provide proof-of-concept for many molecular sensors and molecular memory, for these different spin states or valence tautomers usually have differing magnetic and optical properties.

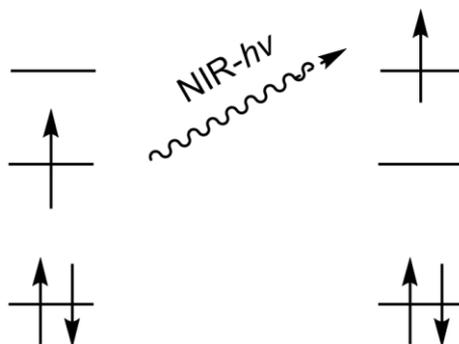


Figure 2 Schematic representation of NIR excitation in a radical containing complex

1.1.2 Optical Properties

In this thesis, optical properties of the studied substances revolve mainly around absorption and related applications. Absorption in liquid solution or in other homogenous medium is commonly expressed by the Beer-Lambert law (*eq. 1*)

$$A = \epsilon cd \quad (1)$$

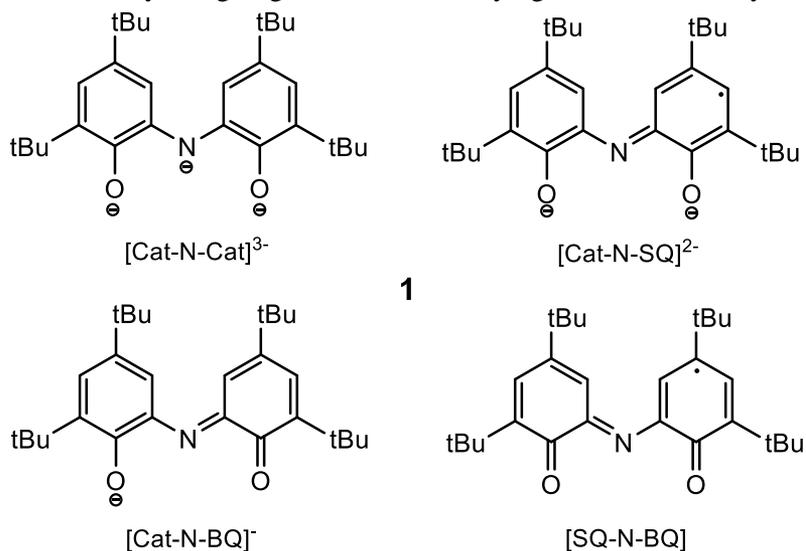
Where A is for absorptivity, which is expressed as a dimensionless figure. The concentration of the sample is c , M or mol/L in its dimensions, and d stands for the path length of the light that travels through the sample. This is commonly 1 cm in standard UV/vis/NIR measurements. Lastly, the molar absorptivity coefficient is ϵ , which is expressed as $\text{cm}^{-1}\text{M}^{-1}$ in its dimensions. The molar absorptivity coefficient represents the studied substance's attenuation of radiation in a given wavelength range.

The definition of the NIR range is not well established, but the infrared (IR) radiation is considered to be longer wavelength than the visible light (400-700 nm) and shorter wavelength than the microwave radiation (1-1000 mm). Thus, the NIR range lies somewhere in the shorter side of wavelengths in the IR range, bordering the visible light range. In this thesis, due to the lack of unambiguous definition for NIR, all wavelengths of electromagnetic radiation that are in the range of 700-2500 nm are referred as 'NIR'.

As discussed formerly, many of the complexes that are studied in this thesis absorb electromagnetic radiation in the NIR range. The NIR absorption is due to the low-energy CT (charge transfer) processes within the complex. In the absorption process, the NIR-photon excites an electron and thus it rises onto energetically higher orbital. Because the energy gap between the ground state and the excited state is low enough, the NIR-photon's given energy is sufficient to excite the electron. Depending on the ligand and the central metal atom, the CT processes may be attributed as MLCT (metal-to-ligand), LMCT (ligand-to-metal) or LLCT (ligand-to-ligand) processes, depending on the complex. It is also well known that the low-energy d-d transitions in the case of square-planar Ni complexes may as well result in NIR absorption. In addition, the *tert*-butyl groups on the *o*-aminophenol moiety are strongly π -electron donating groups. They contribute to the nucleophilicity of the coordinating oxygen and nitrogen atoms as well as function as steric hindrances and thus further stabilize the complex.

1.2 2-[2-Hydroxy-3,5-di-*tert*-butyl-anilino]-4,6-di-*tert*-butyl-phenol

In the late 1960's and in the early 1970's, Stegmann and Scheffler studied various organic-radical forming aminophenols.^{3,4} One of their subjects was the dimerization product of 2-amino-4,6-di-*tert*-butylphenol and its homoleptic tin complex.⁴ Since then there has been numerous studies on the metal complexes that contain this redox-active bis(1-hydroxyphenyl)amine ligand.^{3-5,16-51} In 1975, Girgis and Balch found that homoleptic complexes bearing two bis(1-hydroxyphenyl)amine ligands could be easily synthesized *in situ* by using 3,5-dbtc, metal precursor and ammonia in aqueous solutions under aerobic conditions.⁵ Thus the ligand has drawn chemists' attention due to its electronic properties, namely its ability to have low-lying charge transfer processes and, in theory, four possible oxidation states ranging from 0 to -3 (Scheme 2). This abundance of different oxidation states is very intriguing for chemists studying biomimetic catalysts.



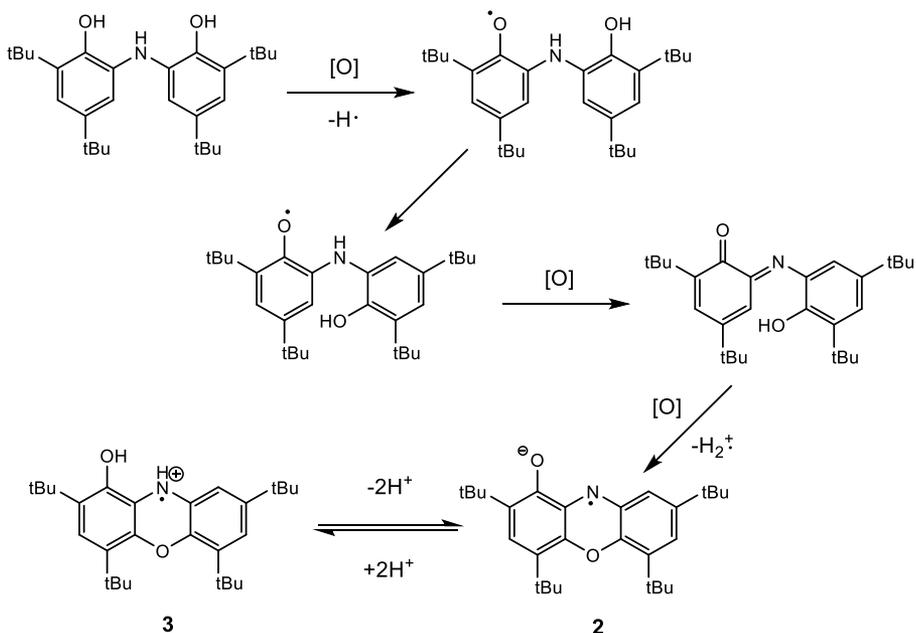
Scheme 2 Possible oxidation states of the deprotonated bis(1-hydroxyphenyl)amine ligand. Adapted from reference.⁴⁸

The ligand **1** coordinates to the metal center as a tridentate ligand and the complexes formed are usually molecular, homoleptic with two principally similar ligands but still may contain an odd electron somewhere on the orbitals of the ligand, depending on a metal center. Group 6 transition metal (Mo, W) ions, with a high oxidation state of 6+, tend to 'consume' all the π -electron donation from the ligands rendering them in (Cat-N-Cat) form.³⁹ For divalent metal ions, for example, Mg^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} and Cu^{2+} , both ligands are in (Cat-N-BQ) oxidation state when the

complex itself is in a neutral molecular form.⁵ In the latter two cases, the homoleptic complex is paramagnetic but the spin moment lies on the metal rather than on the ligands. The complexes' electronic structures are rather complicated and since the original synthesis was repeated and further characterization including redox-reaction studies with EPR, DFT and spectro-electrochemical methods (UV/vis-CV tandem) were done.^{16,17,20,21,24,27,29,49,50} Also years after the original syntheses, some previously hidden isomers have been obtained as in the case of Zn complex²² reported by Wieghardt, *et. al.*, where specific reaction conditions were found to produce a labile, heteroleptic isomer with two organic ligands in different oxidation states.

Another interesting feature regarding the ligand precursor from of **1** is that when the molecule is partially deprotonated and subsequently oxidized, one of the two phenolic oxygens can perform a nucleophilic attack on the aromatic carbon on the opposing phenyl ring (Scheme 3). The formed compound **2** has been studied as a ligand for 3d metal complexes.^{18,47,51} Even though the molecule 'loses' one of its coordinating atoms, it still preserves its redox-active character as a bidentate coordinating ligand. The research has been motivated by the redox activity and the radical character of the ligand as well as possible biomimetic properties of the metal complexes to further clarify the structure of certain metalloenzymes or cofactors.

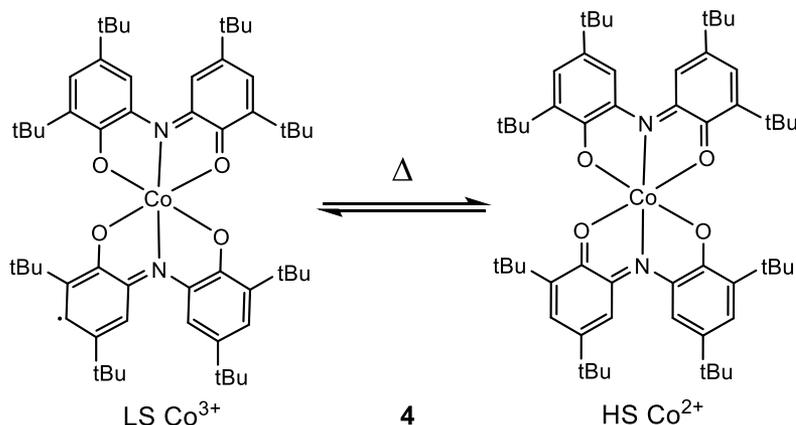
A copper complex with a single tridentate **1** ligand was reported in 1996 and it was found that, at ambient conditions and in pyridine solvent, the oxidation state of the metal precursor was irrelevant regarding the structure of the product.¹⁹ Tetracoordinate copper complexes with a polydentate, redox-active ligand have gained lot of interest among catalyst chemists for their biomimetic properties as metalloenzyme models. For example, galactose oxidase (GO) is known to contain a copper moiety on the active site of the enzyme. Related copper complex has been reported to catalyze, in room temperature, primary alcohol (excluding methanol) oxidation with molecular oxygen as an oxidant.²³ Later on, in the late 2000's and 2010's the studies regarding this ligand and its derivatives in question were more concentrated on heavier and heavier metals, such as, 4d and 5d metal complexes and all the way to the transuranium complexes.⁵² Ta and Zr complexes were studied for their possible use as catalysts in multielectron transfer reactions and to further study the mechanism and metal complex intermediates in those catalytic processes.^{25,26,28,30,33,40} Many articles that have been published during the past decade report mostly basic research revolving around the synthesis and characterization of new complexes with different metal centers^{37-39,43,45} or metal complexes with 1:1 [**1**]-ligand-to-metal ratio, their stoichiometric reactions^{32,34,41,44} and the characterized reaction products.



Scheme 3 Reactions of 2-[2-hydroxy-3,5-di-tert-butyl-anilino]-4,6-di-tert-butyl-phenol leading to the cyclized organic radical phenoxazinolate semiquinonato. Adapted from reference.³

1.2.1 Valence Tautomerization (VT) of the Related Co and Mn Complexes

Transition metal complexes with VT are studied for their potential application as molecular memory, which would provide even more dense means of information storage compared to contemporary devices. VT, in metal organic chemistry, means an intramolecular electron transfer process that may lead to alternative, but stable structure with potentially differing magnetic properties. In such dynamic system, if there is two stable equilibrium states it may be referred as ‘bistability’. This bistability is applicable in nano-scale information storing devices if there is some kind of detectable response to external stimulus, for example, light excitation. There are some conditions that control whether the VT compounds are applicable, *e.g.* both electronic isomers should be stable at ambient conditions. The transformation process between two electronic isomers should be reversible and executed with some relatively simple way, *e.g.* with NIR radiation, and the physical or chemical properties of the electronic isomers should be somehow readable in a reasonably easy fashion.



Scheme 4 The thermally induced VT of the Co complex. Adapted from reference.⁵³

The $[\text{Co}(\mathbf{1}^{\text{Cat-N-BQ}})(\mathbf{1}^{\text{Cat-N-SQ}})]$ complex was first reported by Larsen and Pierpont in 1988.³⁶ Although the complex was extensively characterized, it was approximately a decade later when its thermally induced VT, presented in Scheme 4, in solution was discovered with variable-temperature EPR measurements.⁵³ Interestingly, if the organic ligand contains a bridging oxygen atom between the phenyl rings, the overall structure of the ligand is rigid, which hinders any VT process to take place.³¹ By using an additional reversible redox process, the VT can be converted to an array of four different entities that are interconvertible and differ in their optical and magnetic properties. In practice, this is done by treating the complex **4** with AgBF_4 to obtain $[\text{Co}(\mathbf{1}^{\text{Cat-N-BQ}})_2]\text{BF}_4$.⁵⁴ In a similar fashion, a series of six manganese compounds (three cationic and three neutral complexes) was also prepared, where the metal center appeared in three different oxidation states ranging from Mn^{4+} to Mn^{2+} when heated.⁵⁵ The above-mentioned cobalt complexes, whether in the molecular or in the ionic forms, behaved somewhat similarly in the thermally dependent UV-vis-NIR measurements^{53,54}. This was one of the key measurements to monitor the VT alongside with EPR, SQUID and the Evans' NMR method⁵⁶. The interconversion of tautomers was considered to be an entropy dominated process and the thermal population of electronic isomers is dependent of the Gibbs free energy difference (eq 2).⁵⁴

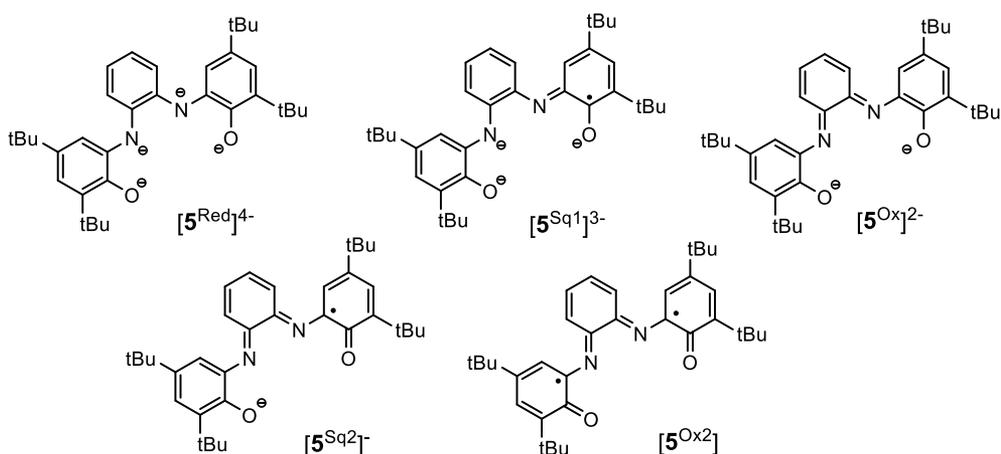
$$G = \Delta G(\text{HS Co(II)}) - \Delta G(\text{LS Co(III)}) = \Delta H - T\Delta S \quad (2)$$

The equation 2 along with the spectroscopically determined thermodynamic quantities (ΔH and ΔS) show that the high-spin Co^{2+} complex is dominant at high temperatures and low-spin Co^{3+} complex is dominant at low temperatures.⁵⁴ The

main difference was that the critical temperature (T_C), which means the temperature where the isomers are equally populated, was higher for the cationic complex when compared to the neutral complex.⁵⁴ For the neutral complex, $T_C = 300$ K.⁵³ In solid state, without any liquid medium, the VT process was found to need drastically higher temperatures ($T_C = 600$ K) to occur and the complexes are thermally decomposed before the isomeric shift is completely finished.⁵⁷ However, these solid-state properties are very much reliant on such things as, for example, solvent molecules in the crystal lattice or different crystal packing modes. This is a tremendous hindrance in developing a functional application for VT utilizing molecular electronic devices.

A more than two decades later from the first observation of its VT, **4** appeared in a couple of materials chemistry applications.^{58,59} In these studies, the cobalt complex' inability to yield, in the solid state as, a suitable VT entity for molecular electronic devices was overcome by a drop-casting procedure. In this technique, the complex was incorporated in PMMA (poly(methyl methacrylate)) which was solvated in dichloromethane and then drop casted on a substrate to form thin films of PMMA with the complex evenly spread into the composite material. The films exhibited similar thermally induced reversible VT behavior at reasonably low temperatures (below the glass transition of PMMA) as the bare complex in solution.⁵⁸ Another successful approach to the same problem was also presented a couple of years later, when toluene solution of the Co complex was used to fill micro-scale polyurethane capsules thus having the compound's properties in solution while getting usability of the solid substance.⁵⁹

1.3 N,N'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine



Scheme 5 The possible oxidation states of the deprotonated N,N'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine ligand. Adapted from reference.⁶⁰

The ligand **5** could very well be considered as the apex of the o-aminophenol moiety containing redox-active ligands as it is known to exist in five different oxidation states (Scheme 5) ranging from the oxidation state of 0 to -4. The electron delocalization may also span over 10 atoms, from one phenolic oxygen atom to another. Thus it has gained some interest over the years and the ligand has proven its effectiveness in homogenous catalysis.^{60,61} The proligand is synthesized and isolated separately, rather than *in situ* to form complexes directly. However, the synthesis is simple, two equivalents of 3,5-dtbc with one equivalent of o-phenylenediamine in a basic hydrocarbon solution at ambient conditions for four days.⁶⁰

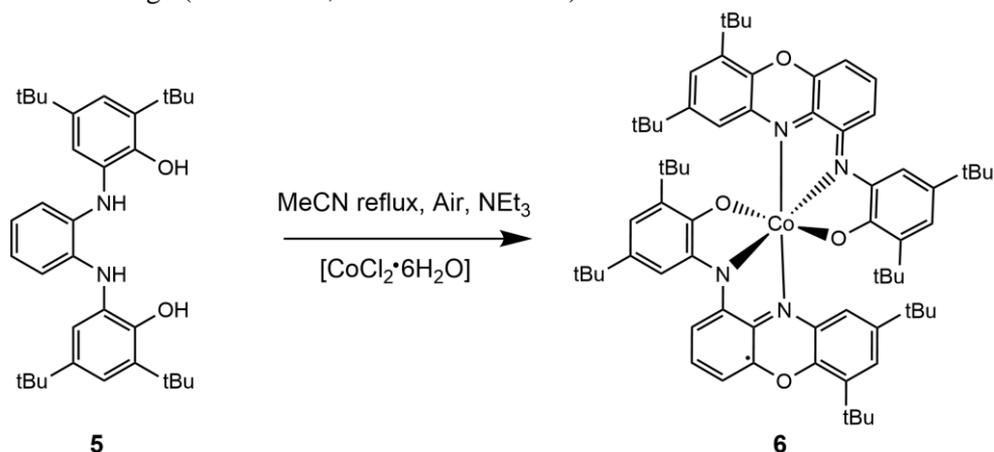
The ligand gained interest when Wieghardt et al. synthesized the Cu and Zn complexes with **5** in four out of five theoretically possible different oxidation states. Most of them were sensitive to air and the molecular Cu and Zn complexes that were studied as homogenous catalysts, had the organic ligand in the fully deprotonated and doubly oxidized **5^{Ox}** form. It was discovered that these Cu and Zn complexes engaged in homogenous catalysis where alcohols were oxidized by the molecular oxygen from the ambient atmosphere. With the tetradentate **5**, the Cu complex was even more effective in aerobic catalytic oxidation of alcohols than the [Cu(**1**)NEt₃] discussed above. The [Cu(**5^{Ox}**)] complex was catalytically efficient, and it also oxidized methanol to formaldehyde, unlike [Cu(**1**)NEt₃].^{23,60}

The electron and energy transfer reactivity of the Cu(**5^{Ox}**) complex have also been studied by reacting it with [Ru(bpy)₃]^{2+*/3+}. It was also discovered that

[Cu(**5**^{Ox})] quenched the fluorescence of [Ru(bpy)₃]^{2+*} by electron transfer from the Cu complex to the excited Ru complex. The reorganization energy was rather high in order to be an effective 1e⁻ redox center. Thus, on the basis of the electron transfer properties of the model complexes, including [Cu(**5**^{Ox})], it was concluded that the galactose oxidase and copper amine oxidase cofactors would have rather slow one electron transfer reactions.⁶²

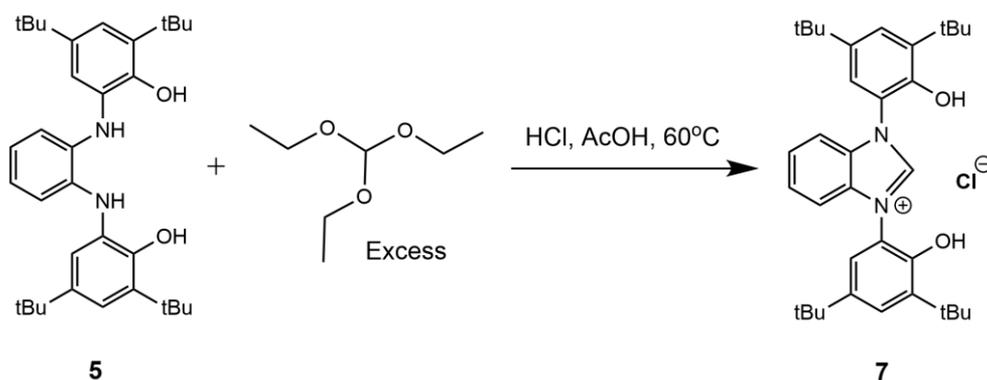
The group 4 transition metal complexes of **5** have also been studied with the interest of developing new lactide polymerization catalysts.⁶¹ In these syntheses, it was found that the alkoxide ligands of the metal precursors played an important role. The sterically hindering [M(O-tBu)₄] yielded complexes with the formula of [M(O-tBu)₂(H₂**5**^{Red})] (M = Ti, Zr, Hf), whereas [M(O-iPr)₄] (M = Ti, Zr) yielded complexes with 1:2 ligand-to-metal ratio, whose were not studied for catalysis. In the case of [Ti(O-iPr)₄], also the mononuclear [Ti(O-iPr)₂(H₂**5**^{Red})] complex could be obtained, if no excess of the metal precursor was used. With an excess of the metal precursor, a [(μ-H₂**5**^{Red})(Ti(μ-O-iPr)(O-iPr)₂)₂] complex was formed. The [Ti(O-tBu)₂(H₂**5**^{Red})] was found to be the most effective polymerization catalyst when compared to analogous Zr and Hf complexes, which is noteworthy, while usually complexes with heavier metal centers of Zr or Hf present higher catalytic efficiencies.⁶¹

Group 4 complexes with doubly oxidized (**5**^{Ox}) ligand have been studied for catalysis in multi-electron transfer reactions.^{63,64} An interesting feature of these complexes with the oxidized ligand^{63,64} is a NIR absorption which is not observed in the alkoxide complexes⁶¹ (discussed above) with the organic ligand in the reduced form. This color change is clearly seen when the yellow [Zr(**5**^{Red})(THF)₃] is oxidized with PhICl₂ to yield dark green [Zr(**5**^{Ox})Cl₂(THF)] which has a strong absorption in the NIR range (λ = 945 nm, ε = 20800 M⁻¹ cm⁻¹).⁶³



Scheme 6 The cyclization of ligands within complexation reaction. Adapted from reference.⁶⁵

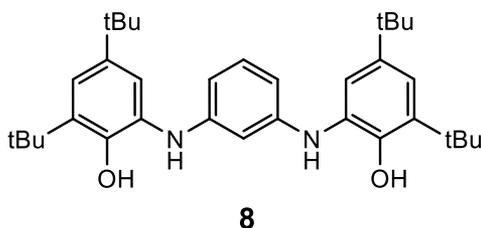
Moreover, the coordinated ligand exist as stable organic radicals, as observed with Co⁶⁵, Mo⁶⁶ and W⁶⁷ complexes with 2:1 ligand-to-metal ratio. In the cobalt complex, the ligands have undergone irreversible cyclization, during the synthesis process (Scheme 6). In each of the three complexes, the unpaired spin delocalized in the orbitals of the organic ligand was verified with EPR and SQUID measurements.⁶⁵⁻⁶⁷ **5** has also been used as precursor to form a heterocyclic carbene ligand⁶⁸ which coordinates to the central metal as a tridentate ligand with two phenolic oxygens and a carbene (Scheme 7). Related transition metal complexes have been studied as catalysts in polymerization reactions^{69,70} and reversible alkyl migration⁶⁸ within the complex.



Scheme 7 Formation of carbene ligand precursor. Adapted from reference.⁶⁸

1.4 N,N'-bis(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-1,3-phenylenediamine

N,N'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,3-phenylenediamine **8** (Scheme 8) has been used as a ligand precursor for binuclear transition metal complexes. Because of its structure, the amino nitrogens are positioned as *meta* substituents on the phenyl ring; the ligand does not have similar 'electronic nimbleness' over the entire molecule as **5** has. But it is still redox-active as a ligand, even though no imino double bonds can form between the nitrogens and the central phenyl ring. Therefore, the *meta* substituent proligand has not gained similar interest as its *ortho* substituent isomer has. The *o*-aminophenol moieties are also more spread out, and this geometrical feature is the main reason why the proligand reacts to form (Mn, Fe and Co) complexes with 3:2 ligand-to-metal ratio.⁷¹⁻⁷⁵

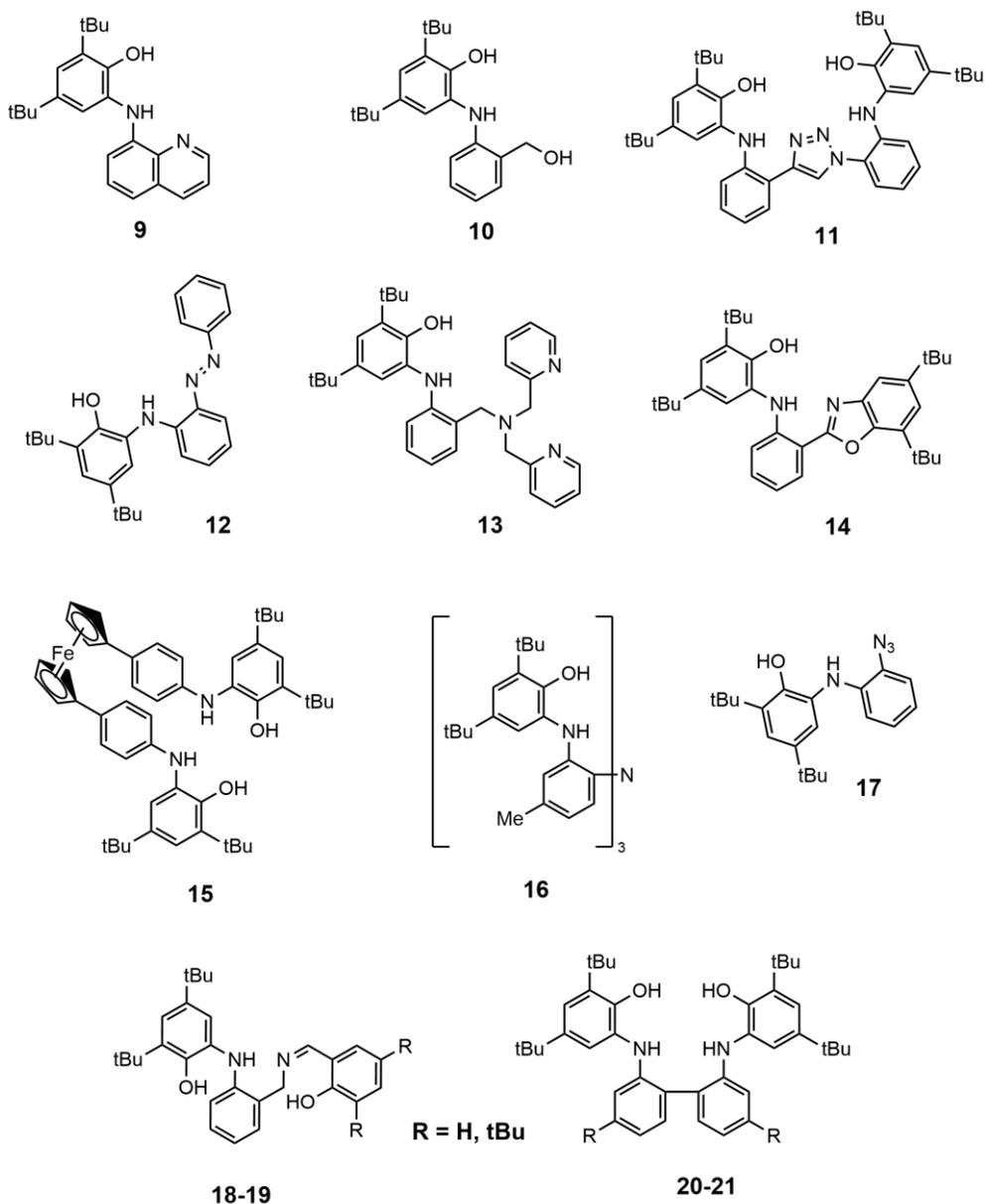


Scheme 8 N,N'-bis(3,5-di-*tert*-butyl-2-hydroxy-phenyl)-1,3-phenylenediamine, adapted from reference.⁷²

These binuclear transition metal complexes have been studied for their magnetic properties, namely for (anti)ferromagnetic couplings between the metal nuclei and/or couplings between the organic radicals that reside on the orbitals of the ligands.^{71,72,75-77} However, the transition metal complexes of *m*-phenylenediamine are studied for catalysis, in catechol oxidation reactions, and as biomimetic model complexes for metalloenzymes with binuclear active sites.^{73,74}

1.5 Other Polydentate Ligands

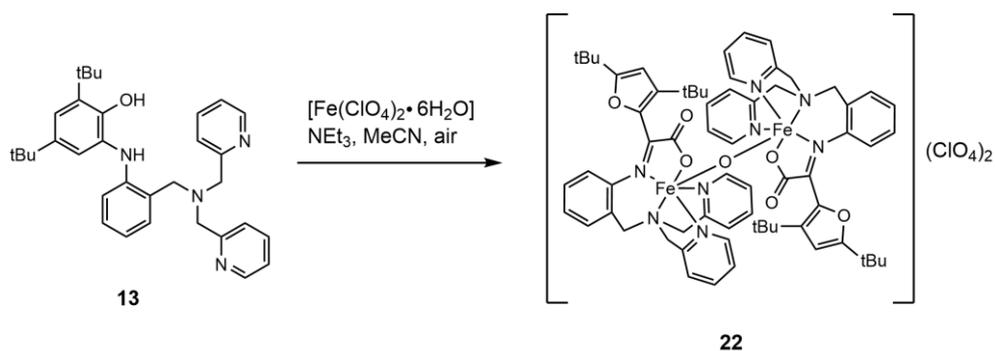
The proligands discussed in this chapter may be roughly divided in two classes: the ones that have the *o*-aminophenol moiety and a pendant arm with some metal-coordinating heteroatom or the others that have two or three *o*-aminophenol moieties connected together with some sort of spacer.



Scheme 9 Proligands. Adapted from references.^{78,80,94,96,82-84,87,89-92}

These proligands have mainly been studied for related transition metal complex synthesis and characterization. However, there are rather interesting curiosities among the literature. The proligand **9** has produced mono- and binuclear 3d metal complexes with redox-active properties.^{78,79} The proligand **10** reacts with MnCl_2 to produce trinuclear complex with Mn nuclei all in different oxidation states ranging from +2 to +4.⁸⁰ A tetranuclear (Cu^{2+})₄ complex with four organic radical ligands is also reported. This tetranuclear complex has shown catalytic activity towards the aerobic oxidation of *o*-aminophenol to 2-aminophenoxazine-3-one.⁸¹

The triazole-spacer bearing proligand **11** has been proposed as a precursor for binuclear mixed-valence Pd complexes where two tetracoordinate Pd nuclei have coordinated to some bridging anion (such as Cl^-) and to the organic ligand via three heteroatoms each.⁸² The proligand **12** reacts with $[\text{Fe}(\text{acac})_3]$ to form antiferromagnetically coupled, LS Fe^{3+} complex with two organic tridentate ligands.⁸³ An interesting feature with the proligand **13** is, that in anaerobic conditions it forms a mononuclear, pentacoordinate anionic complex with Fe^{3+} . In aerobic conditions, however, the proligand forms binuclear complex with a bridging oxygen atom between the metal ions and the *o*-aminophenol moieties have undergone a structural reformation involving a C-C bond cleavage (Scheme 10).⁸⁴



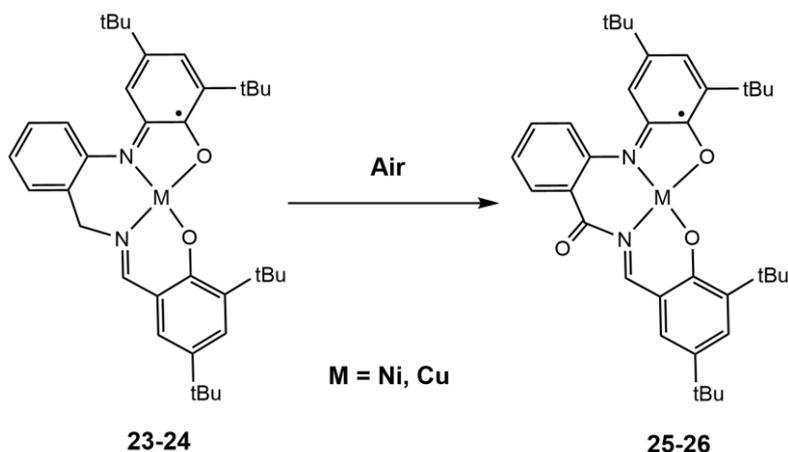
Scheme 10 Aerobical ligand reformation during synthesis. Adapted from reference.⁸⁴

The proligand **14** has been studied as a precursor for metal-organic catalysts. **14** coordinates as a tridentate ligand to form mononuclear complexes with some 3d metal (V, Co, Cu) ions, where 1:1 metal-to-ligand complexes are formed if the metal precursor contains some well-coordinating ligand, such as chlorido, acetato or acetylacetonato ligand.^{85–87} In the absence of coordinating ligands 1:2 metal-to-ligand complex is formed.⁸⁵ However, the reaction of the proligand **6** with $[\text{VOCl}_3]$ affords a vanadyl complex with 1:1 metal-to-ligand ratio and with an additional 2,4-di-*tert*-butyl semiquinonato ligand. This complex has shown catalytic activity

towards oxidation of organic sulfides to sulfoxides.⁸⁸ Cu complexes are studied for aerobic oxidation of primary and secondary alcohol.^{86,87}

To the author's best knowledge, there is only one example on the proligand **15** and as it reacts with $[\text{PdCl}_2(\text{NCPh})_2]$ to form a square-planar complex leaving the ferrocene moiety unreacted.⁸⁹ The proligand **16** forms a heptacoordinated complex with molybdenum⁹⁰ and the proligand **17** reacts with Co^{2+} chloride to form a mononuclear CoCl complex where two ligand precursors' azide moieties have reacted to form a single azo ligand.⁹¹

The proligands **18** ($\text{R} = \text{H}$) and **19** ($\text{R} = \text{tBu}$) both form tetracoordinate complexes with Ni and the ligand substituent effect dictates whether the complex is capable for the aerobic intraligand oxidation reaction (Scheme 11).⁹² Similar reaction has been observed for analogous Cu complex with *tert*-butyl substituents.⁹³



Scheme 11 Ligand oxidation reaction. Adapted from references.^{92,93}

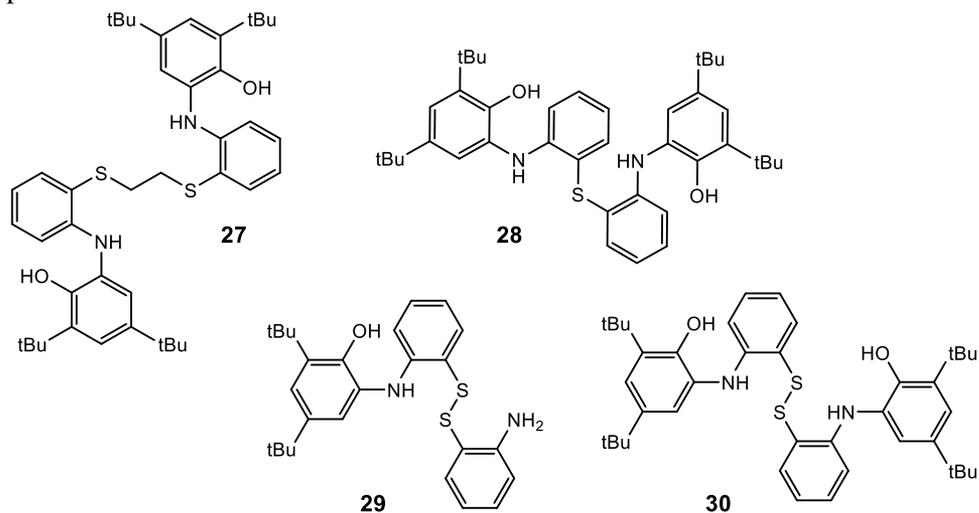
The proligand **20** ($\text{R} = \text{H}$) reacts with various transition metal precursors to form redox-active complexes with a 1:1 metal-to-ligand ratio. However, only the related Cu complex is reported to be catalytically active in alcohol oxidation reactions.⁹⁴

Lastly, the proligand **21** ($\text{R} = \text{tBu}$) has known to react with Mo ^{95,96} and group 10 metal precursors to form complexes with the 1:1 metal-to-ligand ratio. The group 10 (Pd , Pt) complexes have been studied for their hydrogen atom transfer reactions.⁹⁷

1.5.1 Sulfur Containing Ligands

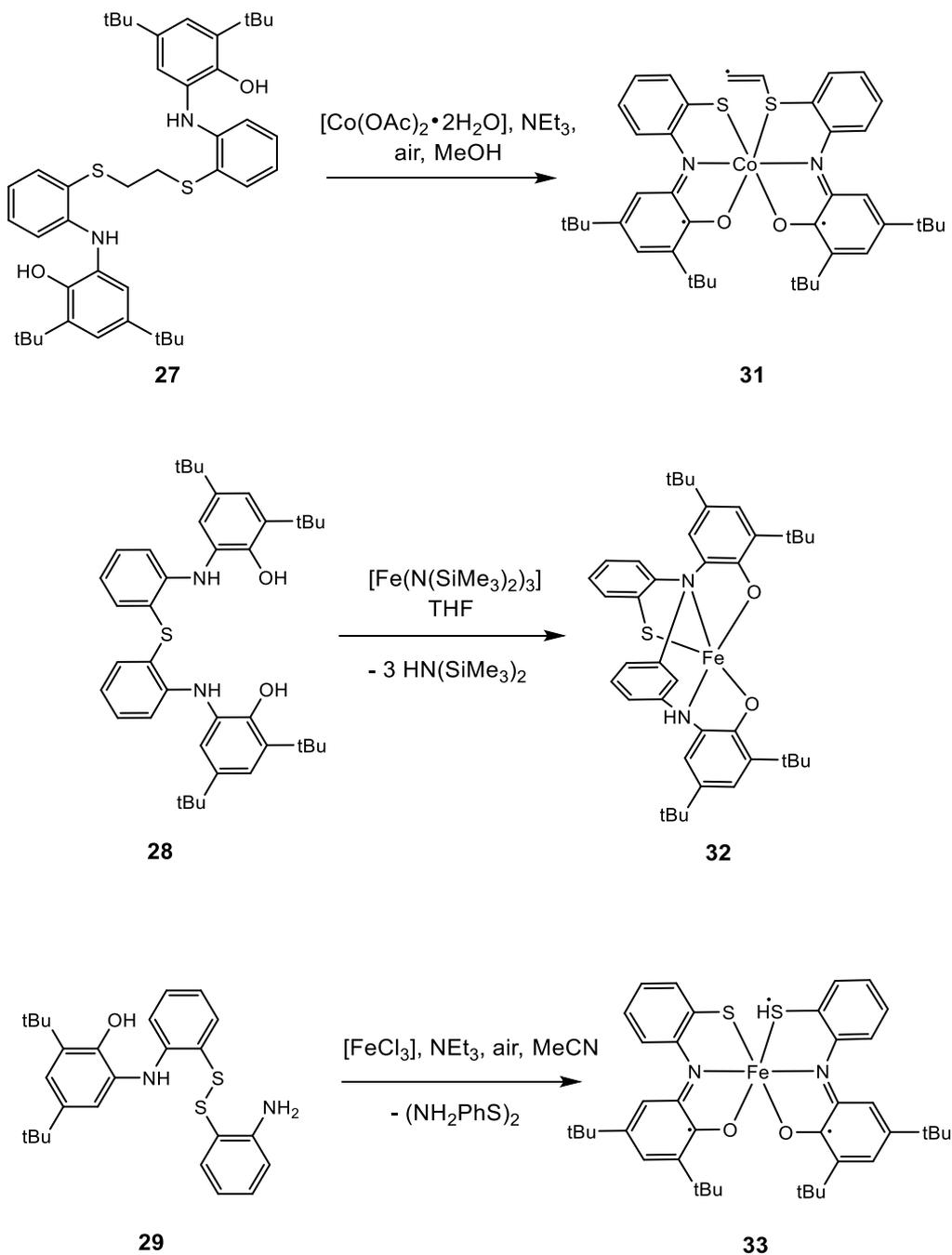
Sulfur is present in many metalloenzymes and thus the motivation arises to research redox-active 3d metal complexes with coordinating sulfur donors. The iron

complexes of the proligand **28**, Scheme 12, have shown catalytic activity as biomimetic models for catechol dioxygenase.⁹⁸ The number of articles related to this subject is rather limited and the articles are mostly about the synthesis and characterization of 3d metal complexes of sulfur and radical containing ligands. Usually, the radical spin lies on the orbitals of the ligand o-iminosemiquinonate moiety, but some other organic radical ligands have been studied (Scheme 13), as well. One interesting aspect in these sulfur containing proligands is the possible cleavage of the sulfur-carbon or sulfur-sulfur bonds of the ligand during the complexation reaction.⁹⁸⁻¹⁰⁰ This has been noted for the proligands **27**, **28** and **29**, presented in Schemes 12 and 13.



Scheme 12 Sulfur containing proligands. Adapted from references.^{70,98,100,101}

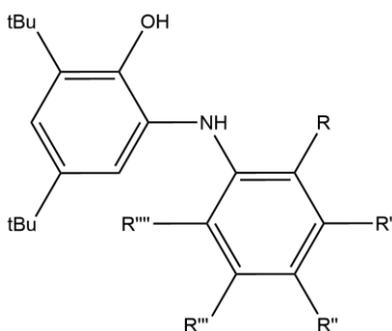
The ligand reorganization, during the complex synthesis, is heavily dependent on the metal precursor. The proligand **27** (Scheme 12) does not undergo sulfur-carbon bond cleavage with Ni precursor⁷⁰ as it does with Co²⁺ acetate dihydrate (Scheme 13).⁹⁹ Likewise, the proligand **28** undergoes ligand reformation in Fe complexation reaction with [Fe(N(SiMe₃)₂)₃] but not with [FeCl₃] as the metal precursor (Scheme 13).⁹⁸ The S-S bond also cleaves during complexation reaction with [FeCl₃] as iron precursor (Scheme 13).¹⁰⁰



Scheme 13 Ligand reformations in the complexation reactions. Adapted from references.^{98–100}

1.6 Bidentate 2,4-di-*tert*-butyl-6-(phenylamino)phenol Derivatives and Their d-Block Metal Complexes

Tens of papers on the complexes of *o*-aminophenolato and iminobenzosemiquinonato ligands (Scheme 14) have been published in the past two decades. The research is most often motivated by homogenous catalysis in order to produce compounds that mimic the active sites of metalloenzymes. The bidentate ligand possesses similar, although limited, redox-active properties when compared to the polydentate ligands that are discussed above. The possible oxidation states of the bidentate *o*-aminophenol ligand range from -2 to 0.



Scheme 14 N-arylamino-phenolato proligand derivatives that are discussed in this chapter. None of the 'R' substituents are coordinating thus the proligand is bidentate.

1.6.1 V, Cr, Mn and Fe Complexes

The related V, Cr, Mn and Fe complexes may possess three organic, bidentate N-aryl-2-aminophenolato ligands in their corresponding protonation and oxidation states, which are dependent on the oxidation state of the metal center. Octahedral Fe and Cr complexes are found to be homoleptic and have three N-aryl-2-imino semiquinonato ligands with trivalent metal centers.¹⁰² In aerobic conditions, the V complex has two fully deprotonated and a one partially protonated ligand, resulting a structure with no odd spins.¹⁰² Also, the Mn complex has three fully deprotonated ligands and two of them are in the partially oxidized imino semiquinonato form. The complex has a Mn⁴⁺ center.¹⁰³ With these complexes, all the radical spins are coupled antiferromagnetically to yield lowest possible ground state for each complex.¹⁰²⁻¹⁰⁴

The related octahedral Fe complexes tend to have a HS Fe³⁺ center, unless the N-aryl moieties of the ligand contain some, strongly electron donating groups, such as *tert*-butyl groups. This renders the complex to be a LS Fe³⁺ complex, at low temperatures, which has a thermally induced spin crossover process.¹⁰⁴ In addition,

there are examples of diamagnetic LS Fe^{3+} complexes with one tetradentate *cis*-cyclam or tren ligand and a one imino semiquinonato ligand whose radical spin is antiferromagnetically coupled with the odd spin of the Fe center.^{105,106}

Tetra- or pentacoordinate Mn^{3+} complexes of 4,6-di-*tert*-butyl-N-(2,6-diisopropyl-phenyl)-o-iminobenzoquinonato coordinate reversibly dioxygen.^{107,108}

Pentacoordinate Fe^{3+} complexes with two N-aryl-2-imino semiquinonato ligands and a (pseudo)halide have imparted their proclivities towards thermally induced spin crossover processes. Interestingly, the tendency for spin crossover is dependent on the coordinated (pseudo)halide and substituent effects of the aniline moiety.^{109,110}

Lastly, a tetragonal, paramagnetic zinc complex with two similar (as discussed before) radical ligands, with spins coupled ferromagnetically, has been reported.¹¹¹

1.6.2 Co Complexes

Cobalt complexes of the bidentate *o*-aminophenolato ligand may have the coordination number of 4, 5, or 6, depending on the number of organic ligands. The correlation between the oxidation states of the complexes and the coordination numbers tend to be rather ambiguous within this class of compounds. Tetra-coordinate Co complexes are typically square-planar^{112–115} and pentacoordinate complexes square-based pyramidal.^{106,113–117} Hexacoordinate complexes, with three *o*-iminosemiquinonato ligands are typically octahedral.

The studies regarding Co complexes are mainly focused on tetra- and pentacoordinate complexes and the interconversion between them. However, hexacoordinate $\text{Co}(\text{o-iminosemiquinonato})_3$ with three radical ligands has been extensively studied and reported.^{102,118,119} Likewise, the substituent effects of the ligand and the effect of redox-activity of the metal center have been studied by comparing the magnetic properties of tris(iminosemiquinonato) complexes of low-spin Co^{3+} and Ga^{3+} .^{120,121} Co complexes had organic ligands with spins ferromagnetically coupled, depending on the substituents on the ligand, although there was no direct correlation between the spin coupling and the π -donating/withdrawing nature of the substituent groups. Though, Ga complexes had radical ligands with their spins antiferromagnetically coupled.^{120,121}

Tetra-coordinate, molecular square-planar Co^{2+} complexes usually have a d^7 electron configuration. However, molecular square-planar Co^{3+} complex with *o*-aminophenol ligands has been reported.¹²² Molecular and ionic square-planar Co complexes have been studied for their catalytic properties in multielectron transfer reactions.¹¹⁴ Also, a square-planar Co^{3+} complex has been reported to participate in homolytic S-S and Se-Se bond cleavage reactions and photocatalytic isocyanate conversion to urea derivatives.¹¹⁵ The related d^7 Co^{2+} square-planar complexes have been studied for their irreversible addition reaction with nitric oxide¹¹⁷ and anti-

fungal properties.¹¹² Pentacoordinate, square-pyramidal Co^{3+} complexes with redox-active ligands do exhibit tendency towards VT, which is quite rare for non-o-dioxolene ligand bearing complexes.¹¹⁶

1.6.3 Cu Complexes

Tetracoordinate copper bis(N-aryl-2-imino semiquinonato) complexes have gained interest over the past years, mainly due to the catalytic activities towards aerobic oxidation of alcohols.¹²³ They have also been studied for their antimicrobial¹²⁴ and antifungal¹¹² properties. However, most of the related literature, concerning the copper bis(N-aryl-2-imino semiquinonato) derivatives, for the most part revolves around the structural and magnetic properties of the complexes.

Substituents of the N-aryl moiety have notable effect on the complexes' catalytic activities. Electron withdrawing substituents, namely $-\text{F}$ and $-\text{CF}_3$, have a favorable effect regarding catalytic alcohol oxidation reactions with related Cu complexes as catalysts. Electron donating substituents, ($-\text{tBu}$ and $-\text{OMe}$) on the other hand, do not pose an impact on the catalytic activities.¹²³

Other, structurally and magnetically significant substituent effects have been studied on the Cu complexes. The copper bis(N-aryl-2-imino semiquinonato) complex with no substituents on the N-aryl moiety is square-planar and has a spin configuration of $(\uparrow\uparrow\downarrow)$, where the odd electrons on the ligands are antiferromagnetically coupled.¹¹⁹ With some *ortho*-substituents in the N-aryl moiety of the ligand, there can be structurally distorting and spin configuration altering effect on the complex.^{125,126} This will render the spin configuration as $(\uparrow\downarrow\uparrow)$. This difference is detectable with EPR spectroscopy, where the spin configurations manifest themselves as either characteristic for a paramagnetic copper moiety $(\uparrow\uparrow\downarrow)$ or an organic radical moiety $(\uparrow\downarrow\uparrow)$. Certain substituents with heavier chalcogens, such as $-\text{SMe}$ and $-\text{SePh}$, have been discovered to alter the complexes' ground state to the organic radical moiety.^{125,126} The $-\text{SMe}$ substituent, when placed at *meta*-position on the N-aryl moiety, does not effect on the spin configuration.¹²⁷ In addition, a $-\text{CH}_2\text{SMe}$ substituent at *ortho*-position will only partially effect on the complex' spin configuration. At low temperatures, the related complex presents a typical Cu^{2+} signal in the EPR studies and at low temperatures the signal is slightly transformed towards an organic-radical signal.¹²⁷ Ligands that have similarly placed oxygen containing substituents ($-\text{OMe}$, $-\text{OPh}$, $-\text{C}(\text{O})\text{OMe}$, $-\text{C}(\text{O})\text{Ph}$) do not alter the spin configuration of the complex from the 'usual' $(\uparrow\uparrow\downarrow)$.^{126,128–130}

The related copper complexes have also been studied as catalysts for trifluoromethylation of silyl enol ethers, heteroaromatics and alkynes by producing CF_3 radicals.¹³¹

Subsequently, the oxidation of the copper bis(N-aryl-2-imino semiquinonato) complex with S-(trifluoromethyl)-dibenzothiophenium triflate yields cationic pentacoordinate complex $[\text{Cu}^{2+}\text{CF}_3(\text{L}^{\text{BQ}})_2]^+$, which is formally Cu^{2+} but it has been noted to function as high-valent Cu^{3+} moiety. The ligands sustain the two-electron oxidation, which is needed for the *umpolung* of the CF_3^+ to transform to a CF_3^- ligand. This complex is found to perform catalytic N-arylated product formation involving carbon nucleophiles.¹³²

1.6.4 Ru and Os Complexes

Ru and Os complexes with N-aryl-2-imino semiquinonato ligands have gained some interest for their redox-active behavior. The studied complexes are mono-¹³³⁻¹⁴⁴ or binuclear^{145,146} but binuclear complexes with N-aryl-2-imino semiquinonato ligands are reported only for Ru. Osmium complexes are less documented. The binuclear structure consists of two N-aryl-2-imino semiquinonato ligands in the ends of the molecule and a bridging tppz ligand. This, well π -conjugated ligand may also be non-innocent and a π -acceptor. These binuclear Ru complexes are studied for their possible intramolecular spin-exchange processes and catalytic properties towards water oxidation reactions.¹⁴⁵

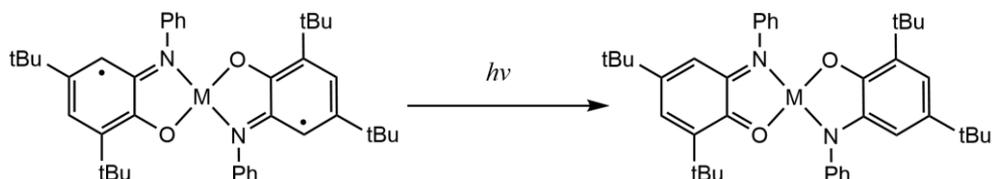
Related Ru and Os complexes may have multiple isolable oxidation states and thus they are a subject of interest in molecular sensing. Potentially hemilabile arene-Ru and arene-Os complexes with a 2-chalcogenidomethylether-N-aryl-2-imino semiquinonato ligand are studied in the pursuit of producing molecular switches.^{136,143}

In addition, there are quite few cases in order to properly compare analogous Ru and Os complexes with NILs.^{133,134,140} Analogous complexes with two bpy ligands and one N-aryl-2-imino semiquinonato ligand have exhibited similar electrochemical and magnetic properties.¹³³ Similar complexes, with two pap π -acceptor ligands instead of bpy ligands, have shown that the Os complexes tend to favor higher, +4 or +3 metal oxidation states,¹⁴⁰ whereas Ru complexes favor +2 oxidation state with a redox-active ligand.¹³⁴ Interestingly, when structurally analogous Ru and Fe complexes with three N-aryl-2-imino semiquinonato ligands are compared, the most distinctive difference is that the Ru complex is diamagnetic¹³⁷ whereas Fe complex has a ground state of $S = 1$.¹⁰²

All in all, particularly Ru complexes with N-aryl-2-imino semiquinonato NILs is a very niche subject but the part that has been studied, is quite extensively and thoroughly studied regarding the synthesis and characterization of complexes and all the possible isolable oxidation states of the complexes along with them. However, Mössbauer spectroscopy proved to be vital in order to discover the essence of diamagnetic complexes with intramolecular anti-ferromagnetic spin couplings.¹³⁷

1.6.5 Group 10 Complexes

Square-planar Group 10 complexes with two N-aryl-2-imino semiquinonato ligands have been subject of interest for their interesting magnetic properties and ability to absorb NIR radiation. Although virtually all metal complexes with corresponding ligands exhibit at least moderate absorptions in the NIR range, Group 10 complexes have proven their superiority in the regard of this property^{106,119,128,147–152}. These strong NIR absorptions are due to the spin- and dipole allowed LLCT processes (Scheme 15).¹¹⁹ For Pt complexes, their molar absorption coefficients can reach up to $\epsilon \approx 7.3 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$.^{119,153} The trend between the central metal atoms and the intensities of absorptions regarding the neutral bis(N-aryl-2-imino semiquinonato) complexes is $\text{Pd} < \text{Ni} < \text{Pt}$.^{119,153} However, these LLCT processes, that appear as intense absorptions, are at their highest when both, the π -donor and the π -acceptor ligands, are N-aryl-2-imino semiquinonato ligands.^{153,154} Pd complexes, with one o-aminophenolato ligand and a bpy ligand, have exhibited lower intensities than the neutral Pd complex with two iminosemiquinonato ligands.^{153,155} Ionic Pd complexes, with two bidentate o-aminophenolate ligands in different oxidation states, have their LLCT absorptions redshifted up to 2000 nm range.¹⁵⁴ Pd²⁺-bis(N-aryl-2-imino semiquinonato) complexes with carboxylic acid groups as para-substituents in the aniline moieties have been utilized as potential NIR absorbing dye sensitizers in DSSCs.¹⁵⁶ To the author's knowledge, this is the sole example of di-*tert*-butyl-o-aminophenol metal complexes to be used in the DSSC application.



Scheme 15 Dipole- and Spin allowed transition. Adapted from reference.¹¹⁹

Coordinating solvent, such as acetonitrile, may quench intense NIR-absorptions with Ni complexes.¹⁰⁶ Interestingly, a dinuclear complex with a Au-Ni bond still exhibits intense NIR-absorption.¹⁴⁸ Thus, it can be concluded that the NIR absorption may not depend entirely on the coordination geometry of the central Ni atom. In addition, the *ortho*-substituent of the aryl moiety has more effect on the NIR-absorption wavelength than the *para*-substituent and both substituents effect NIR-absorption intensities.¹⁵⁰ The Ni complexes with two radical N-aryl-2-imino semiquinonato ligands are typically diamagnetic due to the LS nature of the central metal atom and the antiferromagnetic coupling of the ligands' spins.^{106,119,128,147–152}

Catalytic formation of trifluoromethyl radicals and their application in organic reactions have been reported with Ni^{2+} bis(N-aryl-2-imino semiquinonato) complex. This reaction is mediated through ligand-based oxidation rather than metal centered redox-process.¹⁵²

Structurally analogous group 10 complexes have also been studied with variable temperature $^1\text{H-NMR}$, by measuring the temperature dependence of the chemical shifts, to estimate the magnitudes of the singlet-triplet gaps. The trend between metal centers and π -bonding strength was similar as with intensities of NIR absorptions, $\text{Pd} < \text{Ni} < \text{Pt}$.¹⁴⁷

In addition, singly cationic Pt^{2+} complexes with one iminosemiquinonato ligand and a other bidentate neutral organic ligand have shown intriguing reactivity towards H_2 activation¹⁵⁷ which has been further studied.¹⁵⁸ Also, similar Pt complexes have exhibited reactivity for diolefin oxidation reactions.¹⁵⁹

1.6.6 Other Transition Metal Complexes

With 4d and 5d transition metals as metal centers, the studied complexes have usually one or two bidentate N-aryl-o-aminophenolato ligands. However, there is an example of a homoleptic Mo complex¹⁶⁰ which has three such organic ligands in the aminophenolato form and a central metal ion in the oxidation state of +6.

Group 4 transition metal (Ti, Zr, Hf) complexes, that are prepared with metal alkoxido precursors in anaerobic conditions, tend to preserve two of the alkoxido ligands while two o-aminophenolato ligands coordinate to the metal center. These complexes have known to catalyze lactide polymerization.¹⁶¹

Oxo-rhenium complexes with redox-active ligands react with dioxygen in a dioxygen homolysis reaction. It was also found, that complexes with two N-aryl-o-aminophenolato ligands are more effective in this regard than the similar dicatecholato-oxo-rhenium complexes.¹⁶² Corresponding $\text{O}=\text{Re}$ complexes are also studied for their radical addition reactions.¹⁶³

Lastly, even the rarest of the metals (Rh, Ir) that the crust of the Earth has to offer; have been scavenged to produce complexes with one redox-active ligand. These Cp^*Ir - and Rh complexes with one bidentate N-aryl-o-iminosemiquinonato or N-aryl-o-aminophenolato ligand, have been studied for catalytic dihydrogen oxidation.^{164–166} and for reversible addition reactions.¹⁶⁷ Also, a Rh complex with an additional, coordinative thioether ‘arm’ in the N-aryl moiety of the redox-active ligand, is known to perform VT process.¹⁶⁸ Similar Cp^*Ir complex undergoes a reversible oxidative addition reaction.¹⁶⁷

2 Materials and Methods

The starting complex $[\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}]$ was synthesized by the well-known reaction of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with the excess of 2,4-pentanedione in an aqueous solution using sodium acetate as a base. The product was filtered and washed with water. The N,N' -bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine ligand precursor was synthesized using literature procedures.^{60,64} Other chemicals were used as purchased from commercial sources. The solvents used were of HPLC grade. All syntheses were done under an ambient atmosphere.

The ^1H and ^{13}C -NMR spectra were recorded with 500 Mhz Bruker AVANCE-III NMR system. ESI-MS spectra for complexes were measured in the positive-ion or negative-ion mode with a Bruker micrOTOF-Q spectrometer. The samples were injected as dichloromethane-acetonitrile solutions. Cyclic voltammetry (CV) for complexes were recorded at ambient temperature using a platinum working electrode, a 1 mm diameter platinum counter electrode, and a Ag/AgCl reference electrode. Samples were dissolved in CH_2Cl_2 containing 0.1 M $(\text{Bu}_4\text{N})\text{ClO}_4$ as the supporting electrolyte. The voltammograms were recorded at a scan rate of 100 mV/s or 200 mV/s while the potentials were measured in volts versus the Fc^+/Fc couple. The thermal changes of the complex were studied with TA Instruments SDT Q600 simultaneous TGA-DSC apparatus between 23 and 500 °C in flowing nitrogen gas using an aluminum oxide pan as sample holder and reference. A flow rate of 100 mL/min and a heating rate of 5 °C/min were applied. UV-Vis spectra in CH_2Cl_2 solution were measured with an Agilent Cary 60 UV/vis spectrophotometer in a 10 mm quartz glass cuvette. UV-Vis-NIR spectra were measured of KBr pellets with a Varian Cary 50 spectrophotometer and a blank KBr pellet was used as reference. The solid-state powder EPR spectra were recorded at 18 K using a ESR spectrometer operating at the microwave frequency of 9.030 GHz and 100 kHz modulation of magnetic field. A lock-in amplifier was used for observing the first derivative shape of ESR absorption lines under magnetic field scan. The temperature of samples was controlled using a He-gas flow cryostat. The magnetic properties were measured in a SQUID magnetometer. The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization was measured between temperatures of 2 and 300 K with a Quantum Design SQUID magnetometer MPMS XL with external

magnetic field of $B = 1.0$ T, samples sealed in plastic nonmagnetic straws. The field dependence was measured at 2 K between -2.5 and 2.5 T or -5.0 and 5.0 T using 50 mT steps. Virgin magnetizations as a function of B and magnetic hysteresis curves were recorded in magnetic fields up to 5 T at temperatures of 2, 30, 50, 100 and 300 K. Although the magnetic particles were randomly oriented on the surface of the substrate, the external magnetic field B was always oriented along the out-of-plane axis of the substrate. The photoinduced magnetization measurements were performed in dark or under illumination through an optical fiber with a home-made fiberoptic sample holder attached to the SQUID magnetometer. The samples were drop casted as diethyl ether solutions on circular SrTiO_3 plates (diameter 5 mm). The light source was a Fabry-Perot laser diode by Thorlabs operating at $\lambda = 785$ nm (1.58 eV) with a maximum output power of 10 mW measured at the end of the optical fiber, and hence, the laser fluence on the sample surface was ca. 0.5 mW/mm². The single crystal X-ray diffraction (XRD) analyses were carried out using an Agilent SuperNova microfocuss dual source (Cu/Mo) diffractometer equipped with an Atlas detector. The data collection and reduction, including multifaceted crystal model-based analytical absorption correction, were carried out using the CrysAlis^{pro} program¹⁶⁹. The structures were solved with ShelXS¹⁷⁰ using direct methods and refined on F^2 using full matrix least squares techniques with ShelXL¹⁷¹ within the Olex² (v. 1.2)¹⁷² program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined using a riding model with fixed thermal parameters 1.2–1.5 times the values of the corresponding host atoms (the O–H distances of the O2 and O4 hydroxyl groups were refined freely). The elemental analyses were performed on a Thermo Scientific Flash 2000 instrument

The external quantum efficiency and near-normal specular transmittance of the solar cells was measured with a PV Measurements QEX7 Solar Cell Spectral Response Measurement System in DC mode with no bias light. The current – voltage curves were measured with Keithley 2400 source meter while the cells were illuminated by a solar simulator (Peccell Technologies, Japan, Model PEC-L01) that had been calibrated to 1 Sun (1000 W/m², AM1.5G) light intensity with a calibration solar cell equipped with a KG5 color glass filter (PV Measurements, Inc.) and calibration data traceable to NIST. The dyes were tested in conventional glass-based dye-sensitized solar cells. The semi-transparent photoelectrodes of the cells, having 0.4 cm² active area and $10 - 11$ μm thickness, were prepared by screen-printing a TiO_2 paste (Dyesol DSL 18NR-T) on 2.5 mm thick TEC-15 FTO conducting glass substrates and sintering the printed films at 450 °C for 30 min in air. After this, the photoelectrodes were soaked in the dye solution (0.3 mmol in CH_2Cl_2) for 24 hours in the dark at room temperature. The photoelectrodes did not have compact TiO_2 under layer or light scattering layer. The counter electrodes were made by spreading ca. 4 μl of Pt solution (10 mM H_2PtCl_6 in 2-propanol) on a 2.5 mm thick TEC-15

FTO conducting glass substrates (16 mm x 20 mm) and heating at 390 °C for 15 min. The cells were sealed with 25 μm Surlyn 1702 thermoplastic foil frame. The electrolytes were prepared by mixing the materials at room temperature. The electrolyte was injected in the cell through holes in the counter electrode, which were thereafter sealed with Surlyn thermoplastic foil and a thin microscope cover glass. Reference cells were prepared otherwise identically but using the common reference Ru-dye N719 (0.3 mM in ethanol).

^{57}Fe Mössbauer spectra were recorded with Doppler velocities ~ 3.0 mm/s and calibrated using $\alpha\text{-Fe}$. Spectra were measured in transmission geometry in the temperature interval 77-315 K using an Oxford CF506 continuous-flow cryostat with liquid N_2 as coolant and a $^{57}\text{Co:Rh}$ source (Ritverc Co. 25mCi June 2018). The spectra were fitted using a home-made nonlinear least squares fitting program with the following Mössbauer parameters released in the fitting: the quadrupole coupling constant eQV_{zz} , the relative component intensities, and the isomer shift δ relative to $\alpha\text{-Fe}$. The hyperfine parameters due traces of Fe in the beryllium window of the detector were kept fixed during the analysis. The frozen solution X-band EPR spectra were recorded in $\text{CH}_2\text{Cl}_2:\text{ClCH}_2\text{CH}_2\text{Cl}$ (5:1) at 77 K using Magnostech MiniScope MS 200 spectrometer. Prior to measurements, solvents were dried using appropriate drying methods¹⁷³ and degassed with three freeze-pump-thaw cycles. $\sim 5.0 \times 10^{-4}$ M solutions of samples were used in measurements and they were degassed as described above before the measurements. The following set of parameters were used in measurements: $\nu \approx 9.4$ GHz, centre field (cf) = 3271 mT, spectrum width (sw) = 500 mT, modulation amplitude (md) = 4 mT and microwave attenuation (ma) = 18 dB. Or, parameters were: $\nu \approx 9.4$ GHz, cf = 3291 mT, sw = 500 mT, md = 4 mT and ma = 18 dB. Simulations of spectra were performed with the EasySpin¹⁷⁴ (5.2.28) toolbox for Matlab. All simulated spectra were treated as multicomponent species as the impurity signal with an isotropic g-factor of ~ 2.00 was observed in measured spectra. In both spectra, the main signal was treated as a Fe iron species with $S = 1/2$ and rhombic g-tensors and the impurity signal as a $S = 1/2$ system with an isotropic g-factor. Between the simulated and measured spectrum was obtained by using a rhombic g-tensor ($g_x = 2.15$, $g_y = 2.13$, and $g_z = 1.96$), Gaussian line width (Glw) = 1.36, and weight value (wv) = 1.04 for the Fe species and the isotropic g-tensor = 2.00, Glw = 0.49, and wv = 0.003 for the impurity. Or, similar set of values were used for the Fe species Fe ($g_x = 2.13$, $g_y = 2.10$, $g_z = 1.95$, Glw = 2.20, wv = 1.04) and the impurity ($g = 2.00$, lw = 0.49, and wv = 0.0004) in a simulation. In addition to above parameters, the experimental microwave frequency and centre field were utilized in all simulations. The observed paramagnetic impurity most likely raised from the liquid nitrogen Dewar used in measurements. All DFT calculations were carried out using the PBE0 hybrid exchange correlation functional¹⁷⁵⁻¹⁷⁸ and def2-TZVP basis sets¹⁷⁹. The calculations were carried out using

the *Gaussian 09* quantum chemistry software revision E.01¹⁸⁰. The default integration grid was increased using the “UltraFine” keyword in Gaussian. The geometries of the complexes were extracted from the crystal structure and the positions of hydrogen atoms were optimized at DFT level while the positions of heavier atoms were kept frozen to their crystal structure coordinates. The calculations were carried out on both complexes in the asymmetric unit of the cyclic structure. The calculations were started from a large number of fragment-based initial guesses to account for all reasonable charge and spin configurations of the ligands and the Fe ion. Stability analyzes^{181,182} were then carried out on the optimized wave functions to ensure that they correspond to minima in the variational space.

3 Aims of The Study

The aims of the study were to synthesize and fully characterize various first-row transition metal complexes that would absorb NIR radiation in solution as well in the solid state. Other important goal for this study was to further investigate the produced compounds' potential use in photovoltaic applications, such as, in the DSSC application. This, however, is possible only with a suitable anchoring group within the molecule. There are two structural and fundamental prerequisites for a dye sensitizer molecule in order to function at all:

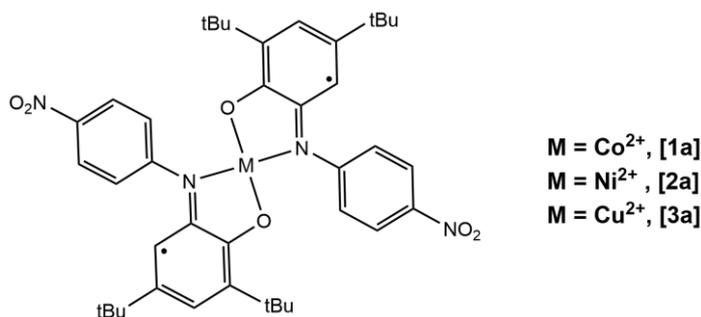
- The (intense) absorption of electromagnetic radiation (vis and NIR range)
- The molecule's adhesion onto the TiO₂ surface of the DSSC and thus ability to act as a dye sensitizer.

Secondary goal was to investigate the compounds' magnetic and potentially NIR radiation induced magnetic alterations, such as dipole- and spin allowed transitions that could lead to differing magnetic properties in the solid state. This feature is potentially usable in NIR sensing materials. Also, thermally induced magnetic transitions, such as, VT or spin crossover processes were subjects of interest.

4 Summary of Results and Discussion

All the complexes were successfully synthesized and isolated in ambient conditions. In all cases, the proligand was prepared separately and the complexation reaction was subsequently executed. The only exception was **3b** (Scheme 18) with structural reformation (article III), as it was prepared from **3a** by refluxing it in basic acetonitrile solution. All complexes were characterized with FT-IR, UV/vis/NIR, XRD, ESI-MS, ^1H - and ^{13}C -NMR (when applicable) and EPR. Also, CV, TGA-DSC, Mössbauer spectroscopy (**3a**, **3b**) and Elemental Analysis (**3a**, **3b**) and SQUID were used to further assess the compounds' properties. In addition, DFT techniques were applied to estimate the detailed structure of the studied complexes. All the results described in this chapter are also included in the published articles. Therefore, it is reasonable to discuss only the relevant main points of the results in this chapter, thus leaving some of the details of the structural characterizations excluded.

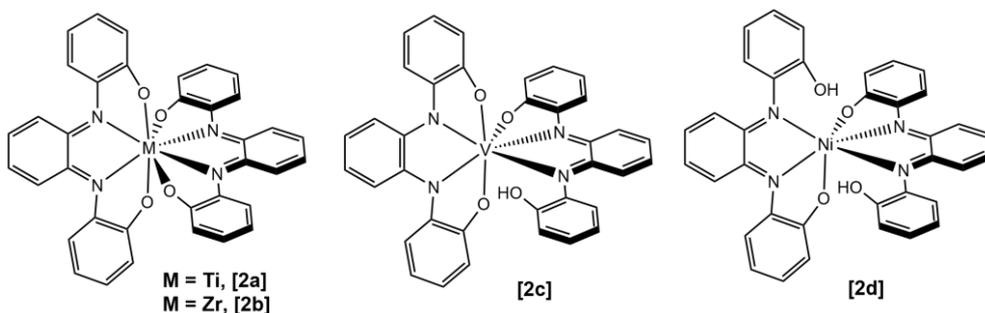
4.1 Crystal and Molecular Structures



Scheme 16 The structure of the complexes in article I. The names that are used of the complexes from hereon in the text are presented on the right in the brackets.

The structural analyses of **1a**, **2a** and **3a** (article I, Scheme 16) and **2a**, **2b**, **2d** (article II, Scheme 17) complexes were straightforward and the structures were determined unambiguously. The complexes presented in article I were close

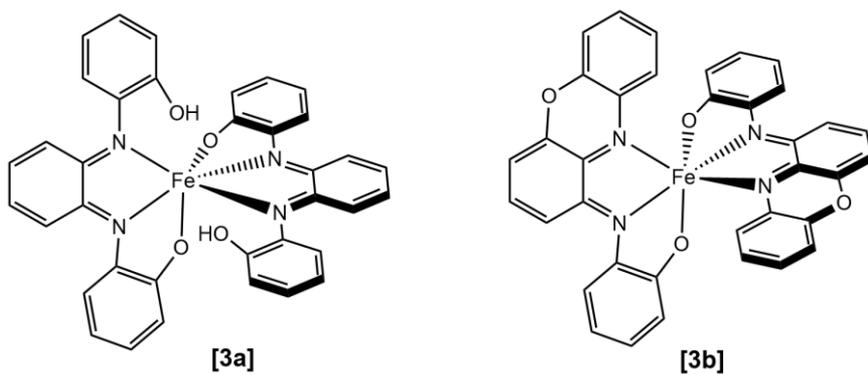
structural analogues to the previously reported compounds.^{113,119} They consist of two radical o-aminosemiquinonato ligands, with ligand radicals' spins antiferromagnetically coupled, and a square-planar M^{2+} ($M = \text{Co}, \text{Ni}, \text{Cu}$) metal center. All of the EPR, SQUID and single crystal XRD studies, as well the NMR for the Ni complex, supported the expectations of the complexes' structures.



Scheme 17 The structures of the complexes in article II. The *tert*-butyl groups of the ligands are omitted for clarity.

2a, **2b** and **2d** too presented rather clear structural determinations, where the single crystal XRD studies exhibited that each of the complexes bear two, either tri- or tetradentate organic ligands that are oxidized and have doubly coordinating, neutral di-imino moieties on the central phenyl ring of the ligands. In addition, the complexes' magnetic properties further supported the XRD results. **2c**, however, had rather elusive structure when compared to the other complexes with similar ligands. From the single crystal XRD measurements it was found that **2c** bore one tridentate and one tetradentate ligand. The tridentate ligand has doubly coordinating, neutral di-imino moiety and one anionic phenolic oxygen coordinating to the central metal with the other phenolic oxygen left dangling uncoordinated, similarly to **2d**. Nonetheless, it was difficult to determine the formal oxidation state of the tetradentate ligand on the basis of bond parameters. According to Brown,¹⁸³ one can use the metrical oxidation state (MOS) to estimate the formal oxidation states of the coordinated o-aminophenol moieties of the studied complex based on the bond parameters, (O-C), (N-C) and the phenyl ring (C-C) bond lengths, of the o-aminophenol moieties. These MOS calculations gave values of $-1.65(12)$ and $-1.79(11)$ for the tetradentate ONNO ligand. The coordinated o-aminosemiquinonato moiety had the calculated value of $-1.10(6)$. These numbers roughly sum up to -4.5 in total for the formal oxidation states of the both ligands. Needless to say, this is somewhat inconclusive and the MOS calculations are known to be more accurate for metal complexes with low oxidation states. Therefore, two alternatives remained while the tridentate ligand is singly anionic, and then the tetradentate ligand should be either quadruply anionic or triply anionic because no cyclohexane-diene di-imino

moiety was detected on the tetradentate ligand. If the central metal is V^{5+} , the molecule should be diamagnetic. NMR, EPR and SQUID measurements along with the DFT calculations provided the information that the samples of **2c** were paramagnetic and had spin densities both on the metal center and on the organic ligand. The complex still was indeed paramagnetic even though it had a V^{4+} metal center and an organic radical spin supposedly antiferromagnetically coupled. The magnetic properties of **2c**, however, were somewhere in between the diamagnetic $S = 0$ state and the paramagnetic $S = 1$ state. Thus, the detailed electronic structure of **2c** remained somewhat unclarified. One could also speculate that the composition of the samples consisted of both $S = 0$ and $S = 1$ spin state complexes.



Scheme 18 The structures of the complexes in article III. The *tert*-butyl groups of the ligands are omitted for clarity.

3a and **3b** (Scheme 18) described in the article III presented an interesting case. The bond parameters from the single crystal XRD seemingly indicated that **3a** has two identical tridentate monoanionic ligands and a LS Fe^{2+} metal center. The DFT calculations provided the information that the complex actually was a LS Fe^{3+} complex with a single antiferromagnetically coupled spin that was delocalized over the two organic ligands. **3b**, on the other hand, was found to possess a HS Fe^{2+} metal center in the crystalline state. As it will be subsequently discussed, the crystals of **3b** ‘lost’ 25 % of their paramagnetic spin moment in low temperatures. The XRD measurements at 95 K reveal that the asymmetric unit contains four molecules. Three of them have Fe-N bonds ranging from 2.064 to 2.157 Å and Fe-O bonds ranging from 1.997 to 2.019 Å. Then, the one has Fe-O bonds of 1.955 and 1.961 Å and Fe-N bonds ranging from 1.904 to 1.987 Å. Rather obviously, the phenolic oxygens are similarly anionic in both cases and thus do not differ in Fe-O bond lengths but the Fe-N bonds are shorter within the diamagnetic Fe molecule due to the increased anionic nature of the nitrogen atoms. The MOS calculations give -1.12(6) and -1.09(7), which roughly sum up to -2, to the o-imidosemiquinonato moieties of the ligands of the major component in the asymmetric unit. The MOS calculations for

the minor component give values of $-1.33(2)$ and $-1.20(1)$, which is in the direction of -3 (-2.53) but still seems somewhat inconclusive at the first glance. However, this may indicate that the coordinated nitrogens on the phenoxazinyl moieties do also bear some anionic nature which is regrettably excluded from these calculations. Especially, when the corresponding Fe-N bond lengths are *ca.* 0.15 \AA shorter in the minor component. Furthermore, the Mössbauer experiments of the crystalline sample of **3b** exhibited two components at low temperatures (77 K) with an integral ratio of 1:3. The minor component gradually merged with the major component at higher ($T > 100 \text{ K}$) temperatures.

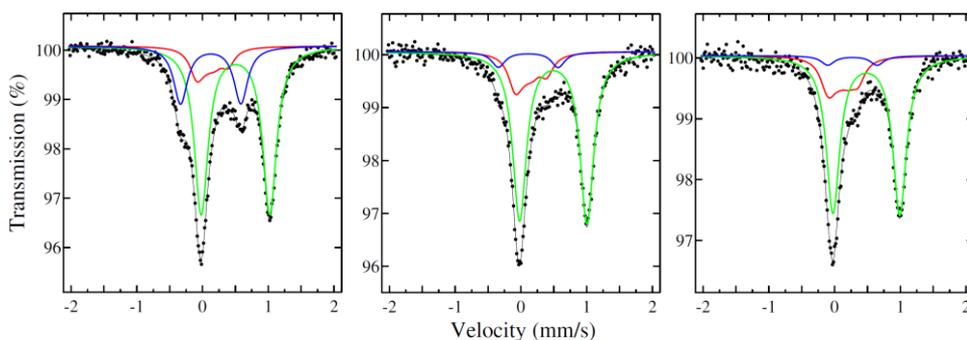
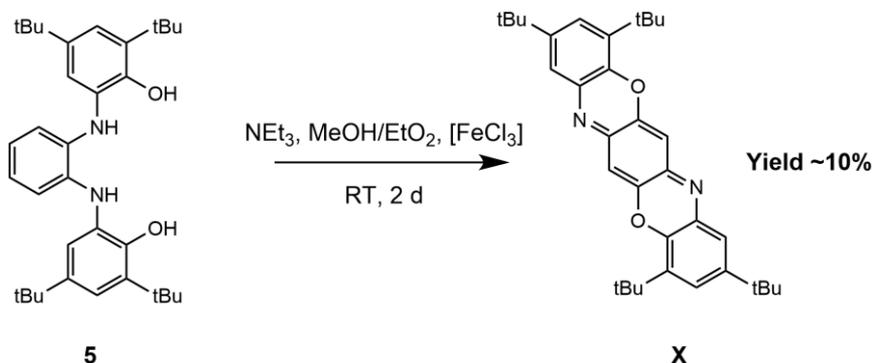


Figure 3 Mössbauer measurements for **3b** at different temperatures, 77 K (*left*), 110 K (*center*) and 140 K (*right*). The green component is the major, HS Fe^{2+} , the blue is the minor component, LS $\text{Fe}^{2+/3+}$ and the red component is iron impurity in the Mössbauer apparatus.



Scheme 19 Obscure proligand transformation reaction.

Lastly, an interesting and reproducible side reaction was observed in an attempt to synthesize **3a**: 0.967 mmol of **5** with slight excess of $[\text{FeCl}_3]$ and a catalytic amount of NEt_3 were dissolved in 50 mLs of MeOH/EtO_2 mixture, in a 3:2 ratio, respectively. The reaction mixture was left to stand for two days at room temperature

in an open vessel. Orange, plate-like crystals of **X** isolated from a dark purple mixture and washed with MeOH. **X** was not obtained when an excess of NEt₃ was used. **X** was found to be paramagnetic, and luminescent in solution. XRD measurements revealed that **X** was recently reported,¹⁸⁴ although after a different synthesis. The synthesis path itself (Scheme 19) is puzzling and incomprehensible. However, the study and the speculation of this reaction path is well beyond the scope of this thesis and therefore is mentioned here as a curiosity due to its novelty.

4.2 Optical Absorption Properties of the Compounds and Their Applications

All complexes displayed significant absorptions in the NIR range. Only **2c** did not have an absorption maximum in the NIR range but rather a broad absorption tailing in the NIR range. As discussed earlier, the strong NIR absorptions may occur due to several reasons, which are low-lying LMCT, MLCT or LLCT processes. Also, d-d transitions, especially with Ni complexes, have to be considered when one is trying to reason the origin of the absorptions. The absorptions of all studied molecules are shown in Figs.4-6 as molar absorption coefficients in the function of wavelength. The absorptions in the NIR range are in each case high, molar absorption coefficients ranging from 5000 to 27000 $M^{-1}cm^{-1}$. The solid-state UV/vis/NIR spectra in KBr pellets resulted similar absorption to those measured in solutions.

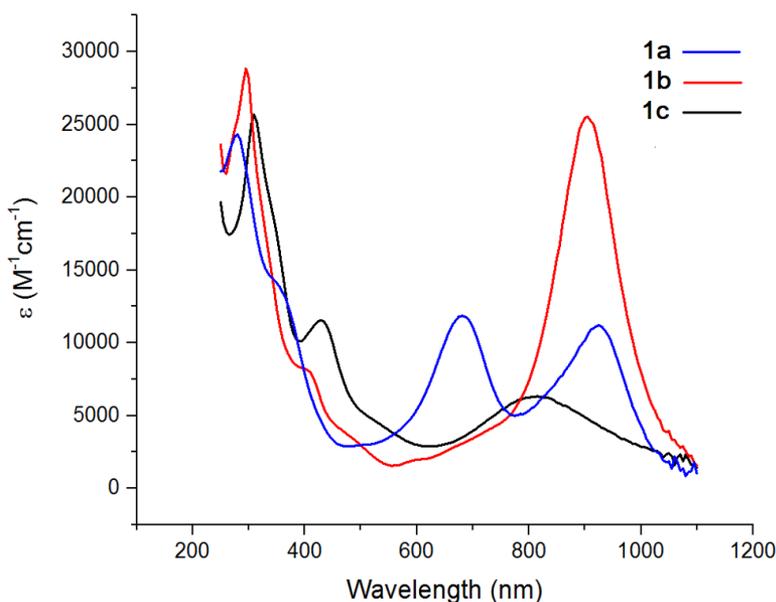


Figure 4 UV/vis/NIR spectra of complexes studied in article I. Samples were dissolved in CH_2Cl_2 and measured at RT.

These absorption properties were subsequently studied with SQUID by illuminating the samples in various temperatures and magnetic fields. The samples were prepared by dissolving complexes in diethyl ether and placing them on a $SrTiO_3$ plate in a dropwise manner. Regrettably, non-compatible absorptions rendered the complexes in article I unusable in this experiment, where the samples were illuminated with 785 nm wavelength laser. These complexes were studied as

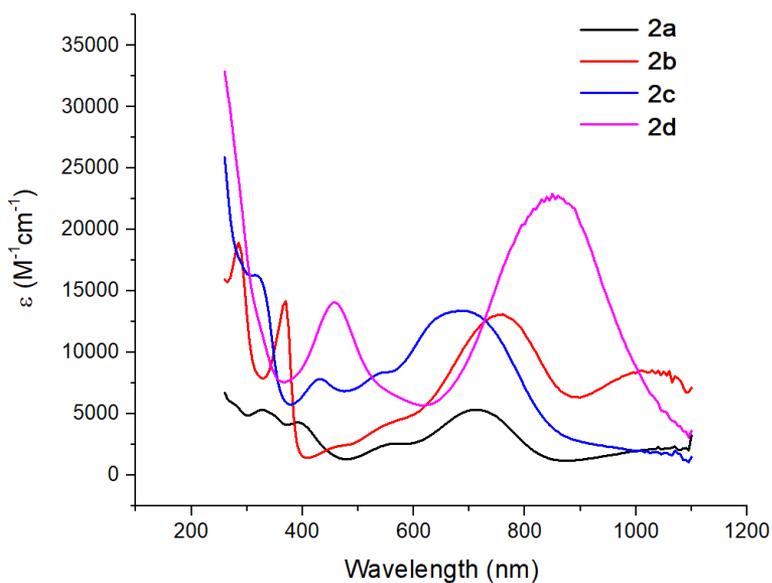


Figure 5 UV/vis/NIR spectra of complexes studied in article II. Samples were dissolved in CH_2Cl_2 and measured at RT.

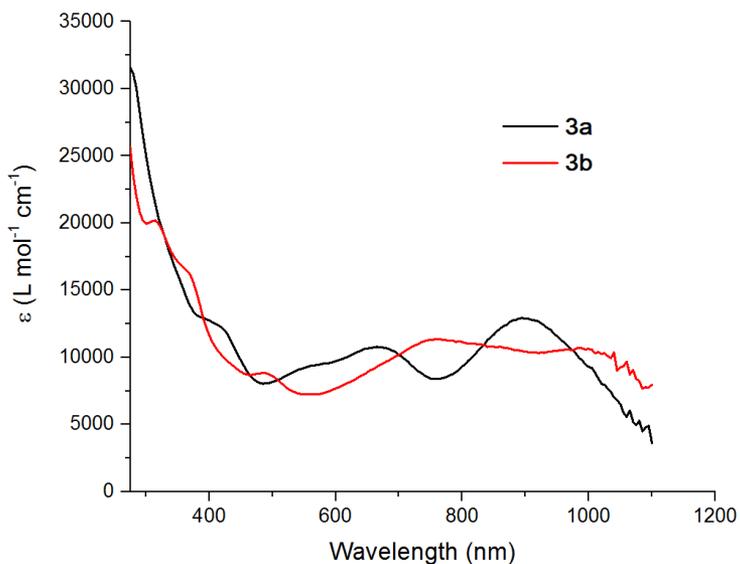


Figure 6 UV/vis/NIR spectra of complexes studied in article III. Samples were dissolved in CH_2Cl_2 and measured at RT.

possible dye sensitizers for DSSC application. Nitro group had been reported to be

a viable anchoring group in dye sensitizer molecules.¹⁸⁵ However, it was later on found that the nitro group provided insufficient adhesion to the TiO₂ surface.

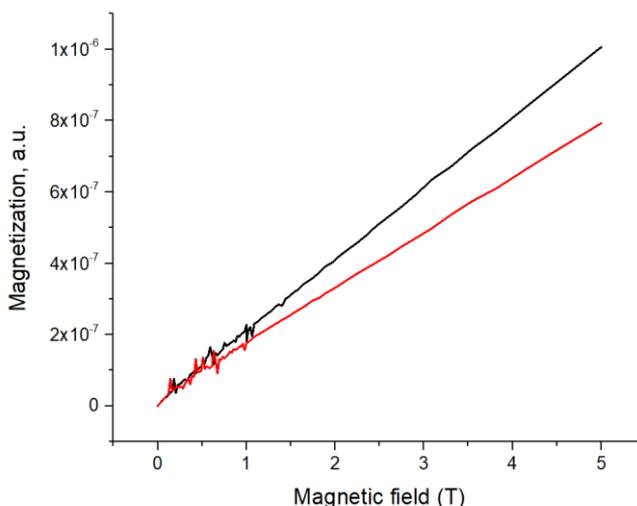


Figure 7 The measured virgin curves of **2c** on a SrTiO₃ disk at 100 K. The red curves result from the measurements done under irradiation in the NIR region, and the black curves are from the measurements done without irradiation.

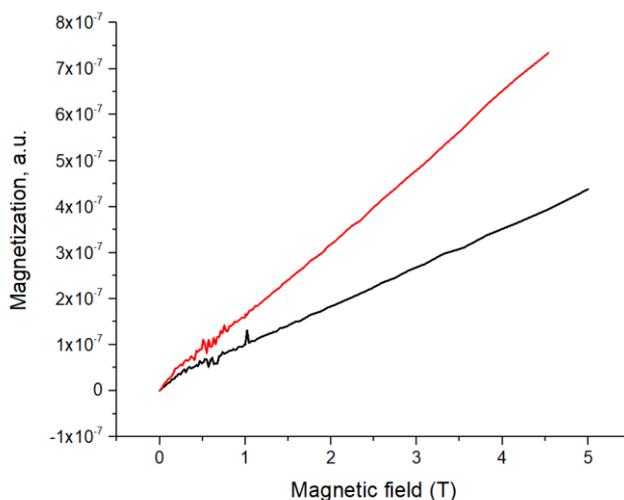


Figure 8 The measured virgin curves **2d** on a SrTiO₃ disk at 100 K. The red curves result from the measurements done under irradiation in the NIR region, and the black curves are from the measurements done without irradiation.

From the studied compounds, **2c**, **2d** and **3b** exhibited transitions that resulted in differing magnetic properties when illuminated. With **2d** and **3b**, the total spin moment was increased when the sample was illuminated. With **2c**, on the other hand, the total spin moment of the sample was decreased. This indicates that in each of

these cases, a spin-forbidden transition or a VT process occurs. Although heavily absorbing, in the 785 nm range, **2a**, **2b** and **3a** probably have dipole- and spin allowed transitions that do not result in paramagnetic excited states when the complexes are illuminated.

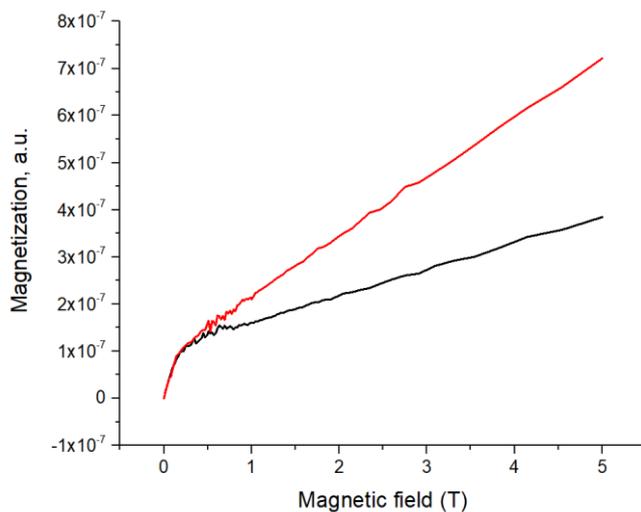


Figure 9 The measured virgin curves of **3b** on a SrTiO₃ disk at 100 K. The red curves result from the measurements done under irradiation in the NIR region, and the black curves are from the measurements done without irradiation.

4.3 Magnetic Properties of the Complexes

As discussed before, the **1b**, **2a**, **2b** and **3a** are diamagnetic and thus excluded from this chapter's discussion. **1a**, **1c** and **2d** were considered as metal-centered paramagnets, where the **2d** was clearly a HS Ni²⁺ centered Curie-type paramagnet without any organic radical spins. **1a** and **1c** were in turn systems where the organic radical spins have coupled antiferromagnetically leaving the spins of the central metals to determine the complexes' paramagnetic properties. However, the EPR and SQUID results would suggest that some delocalization of spin density does occur between the metal center and the organic ligands. In the case of **1a**, the exact magnetic properties were difficult to determine due to the zero-field splitting.

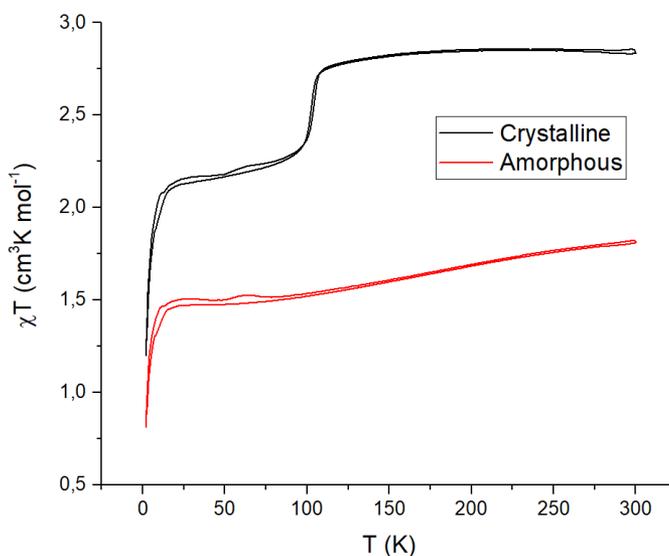


Figure 10 The molar susceptibility of **3b** times temperature in the function of temperature expressed in cgs units.

3b was the only example on the studied complexes that exhibited any kind of thermally induced spin-crossover or VT behavior. Two different samples were prepared, a one crystalline, where the substance was recrystallized from EtO₂/MeOH mixture and an amorphous sample, that was purified by similar recrystallization, dissolved in hexane, filtered and rapidly evaporated by rotary evaporator. As exhibited in Figure 10, in the crystalline state, **3b** undergoes a magnetic shift at *ca.* 100 K, where the total spin moment alters. When the crystalline sample is cooled below 100 K, the χT value decreases *ca.* 25 %. This is in accordance with the low-temperature XRD and Mössbauer results of the crystalline sample. However, the amorphous sample exhibits substantially different magnetic properties. There can be

observed a gradual rise in the χT value, from *ca.* 80 K, when the sample is heated but the χT value is significantly lower all the way. The field dependence, of the crystalline sample, has a value of *ca.* $2.1 N_{\text{A}}\mu_{\text{B}}$ at 2 K in 5 T magnetic field (Fig. 11), which is in a good agreement with the spin-only value of HS Fe^{2+} , $S = 2$. The field dependence value is lower with the amorphous sample, *ca.* $1.5 N_{\text{A}}\mu_{\text{B}}$ at 2 K in 5 T field. Therefore, we can conclude that in some cases, the magnetic properties of the sample are heavily dependent on the crystal packing of the sample and intermolecular effects.

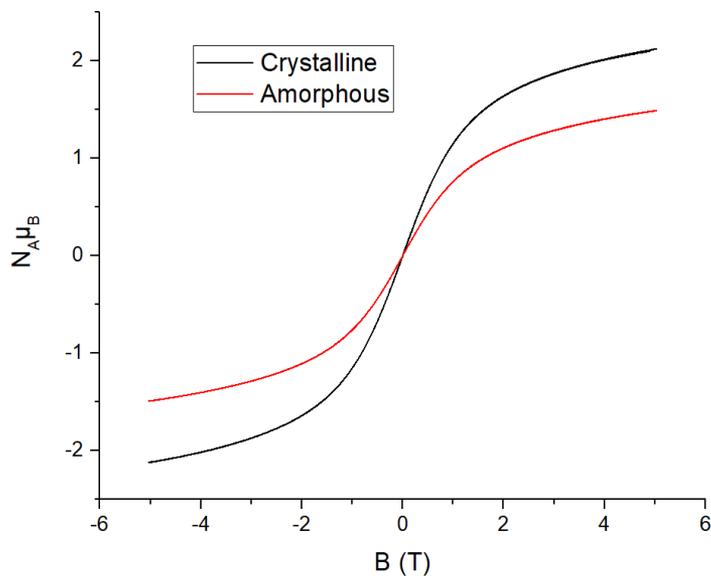


Figure 11 The field dependence of **3b** complex measured at 2K.

4.4 Summary and Conclusions of the Results

All synthesized complexes were NIR absorbing and they were extensively characterized. The nitro group did not provide adhesion on the TiO₂ layer thus the nitro-containing complexes did not function as dye sensitizers. Efforts were made to prepare similar complexes with carboxylic acid anchors but those syntheses resulted in insoluble, probably oligomeric materials or substances that were otherwise hard to extract as crystalline, pure compounds.

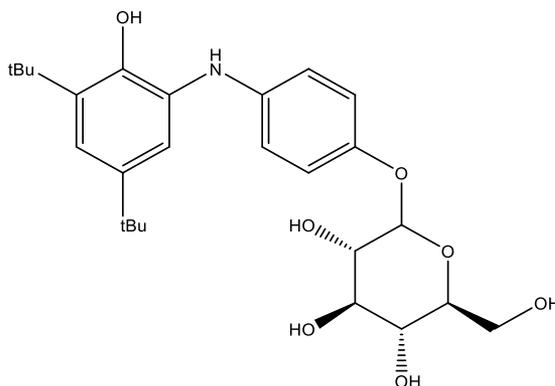
Three complexes (**2c**, **2d**, **3b**) underwent, in the solid state and in the presence of an external magnetic field, a transition that altered the complexes' magnetic properties when illuminated with a 785 nm laser beam. This raises hopes in pursuit of NIR-detecting materials and –sensors.

The other complexes (**2a**, **2b**, **3a**) that did not present any transition in the magnetization studies, however presented interesting examples of redox-active transition metal complexes and thus comparison for the paramagnetic complexes that underwent magnetic shift when illuminated. Also, **2a** as an octacoordinated Ti complex, is a somewhat unusual case.

All in all, the 4,6-di-*tert*-butyl-*o*-aminophenol moiety (or moieties) containing organic molecules perform well as ligand precursors in order to produce stable and molecular NIR absorbing complexes with various transition metal precursors. Some of those complexes may provide interesting interchangeable optical and magnetic properties, which in turn may powerfully depend on the purity and the crystal packing of the solid state material.

5 Summary, Conclusions and Future Speculations

The redox active complexes with NILs have gained a lot of interest during the past decade. However, even though the studied complexes have interesting features, such as, NIR absorption and elusive magnetic properties, *i.e.* possible tendencies towards bistable compounds. Probably the most noteworthy achievements to date, with related complexes, have been obtained in the field of homogenous catalysis,^{23,60,123} mainly with Cu complexes. The amount of existing literature has expanded but most of the articles published revolve around the synthesis and characterization of ‘novel’ compounds.



Scheme 20 Proposed structure for a ligand precursor.

In the Author’s opinion, the related future research should concentrate more on one of two objectives: first, to produce (pro)ligands with a ‘non-innocent’ moiety and an additional functional group attached to the ligand in order to combine two useful and co-operating properties in one compound. For example, β -glucosyl group combined with non-innocent and coordinating *o*-aminophenol moiety (Scheme 20) could provide useful compounds. The described proligand could function as a precursor for anti-cancer treatment where complexes with redox-pair having metal centers^{186,187} (Fe, Cu) and redox-active ligands would cause oxidative stress to target

cells. The ligand's carbohydrate group would help to direct the complex straightforwardly to the cancer cell. The suggested ligand precursor is exhibited in Scheme 20. Similar, square-planar Co complex could be studied for water-splitting reactions¹⁸⁸ because the carbohydrate group would downgrade complex' hydrophobicity. The β -glucosyl group would also function as an anchoring group and adhere to TiO₂ surface in DSSCs via hydrogen bonding, so various metal complexes could be utilized as NIR absorbing photosensitizer dyes.

Second objective should be to study oligo-/polymeric structures that would form materials that then would utilize the characteristic properties that redox-active complexes possess. These properties are electron transportation/conductivity, NIR absorption, bistability with differing magnetic properties, ferromagnetic coupling between spins, materials with magnetic anisotropy and catalytic properties.

Therefore, it may be reasonable to study metal-organic polymeric structures in heterogenous catalysis to have a 'compromise' between inorganic heterogenous catalysts and mononuclear metal complex homogenous catalysts. Alternatively, to study the NIR-photocatalytic properties of those same structures.

However, there are some possible hindrances or pitfalls regarding these studies. As early as in 1994, there were noted concluding remarks as such: "We are currently attempting to design a bistridentate radical anion, able to bridge two different diamagnetic or paramagnetic metal ions, thus yielding a sequence of ferromagnetically coupled paramagnetic moieties."¹⁶ In 2020, no metal organic polymers where o-aminophenol moieties act as complexing agents, to the author's knowledge, have been published. This could mean that linear structures are hard to obtain. Which would mean that metal-organic conductors or -ferromagnetic materials, at least with bistridentate proligands, would not be easily obtainable. It is possible, that (bis)bidentate or bistridentate proligands would react with metal precursors to form cage-like, spherical¹⁸⁹ structures which would render the material to be unusable in conducting or ferromagnetic applications.

If so, perhaps these oligomeric materials could be utilized in a different way. For example, 4,4'-diamino-stilbene can react with two equivalents of 3,5-dtbc to form a (bis)bidentate proligand. The metal-organic cage-like structures subsequently produced would then have bridging ligands with *cis-trans* isomerism which could be altered by light excitation. By thus altering the dimensions of the 'cage', it could be possible to have also differing magnetic or optical properties within the material. This would then be used in the applications of molecular sensing or molecular memory. In addition, similar structures without this *cis-trans* isomerism could be studied for thermally, pressure or photonically induced VT for similar purposes.

In conclusion, the topic of synthesis and characterization of the related o-aminophenolato- or o-iminosemiquinonato ligands bearing, mononuclear, molecular metal complexes seems to be rather 'chewed up'. I feel that the information that has

been accumulating over the years, regarding mono- and binuclear complexes with NILs, would be put into the best use possible by studying novel metal-organic polymeric materials, their properties and applications. There are things to investigate in the regard of oligomeric photoactive metal-organic materials or heterogenous catalysts. Of course, other potential applications even for mononuclear complexes with NILs may emerge, but only if someone is exploring them.

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