

### SULFO-FUNCTIONALIZED ARYLHYDRAZONES OF ACTIVE METHYLENE COMPOUNDS AS A PROMISING LIGANDS FOR INORGANIC SYNTHESIS

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# Química

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# ABSTRACT

A new monomer,  $[Mn(H_2O)_6][HL^{1a}]_2 \cdot 4H_2O$  (1), and a new tetramer,  $[Cu(H_2O)Cu(H_2O)_4(\mu \cdot L^2)]_2 \cdot 2H_2O$ (2), were obtained by reaction of  $Mn(CH_3COO)_2 \cdot 4H_2O$  and  $Cu(NO_3)_2 \cdot 2.5H_2O$  with 2-(2-(dicyanomethylene)hydrazinyl) benzenesulfonate (**NaHL**<sup>1</sup>) and 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-4-hydroxybenzene-1,3-disulfonate (**Na<sub>2</sub>H<sub>2</sub>L**<sup>2</sup>), respectively. Template condensation of NaHL<sup>1</sup> with water on manganese(II) acetate tetrahydrate led to a new ligand, HL<sup>1a</sup> = 2-(SO<sub>3</sub><sup>-</sup>)-C<sub>6</sub>H<sub>4</sub>-(NH)N=C(C=N)[C(=O)(NH<sub>2</sub>)], derived from nucleophilic attack of water (a) on a cyano group of NaHL<sup>1</sup>. These complexes were fully characterized by IR, elemental analysis and X-ray diffraction methods.

A new resonance assisted hydrogen bond (RAHB)-driven reaction was found in the interaction of 3aminocrotononitrile with the diazonium salt of 2-aminobenzenesulfonic acid in basic medium, leading to (*Z*)-2-(2-(1-cyano-2-oxopropylidene) hydrazinyl)benzenesulfonate (**NaHL**<sup>3</sup>). A new method for the synthesis of an Ag<sup>l</sup> complex with arylhydrazones of methylene active compounds

(AHMAC) ligands was found in the reaction of silver(I) nitrate with NaHL<sup>3</sup> in HNO<sub>3</sub> medium. Two new copper(II) complexes,  $[Cu(H_2O)_2(en)_2]^{2+}[(HL^3)^-]_2$  (**3**) and  $[Cu(en)_2(\mu-L^3)^{2-}]_{2n} \cdot nH_2O$  (**5**), and a silver(I) complex,  $[Ag_2(\mu-HL^3)_2]_n \cdot nH_2O$  (**4**), were isolated from reaction of NaHL<sup>3</sup> with  $Cu(NO_3)_2 \cdot 2.5H_2O$  and AgNO<sub>3</sub> in the presence of ethylenediamiane (en) and HNO<sub>3</sub>, respectively. All these complexes were characterized by elemental analysis, IR spectroscopy and X-ray analysis. The nuclearity and supramolecular arrangement of the obtained compounds depended on the metal atoms and the reaction conditions.

The new complexes (1-3) exhibited high catalytic activity for the solvent- and additive-free microwave (MW)-assisted oxidation of primary and secondary alcohols with *tert*-butylhydroperoxide, leading to yields of the oxidized products up to 85.5 % and turnover frequencies (TOFs) up to  $1.90 \times 10^3 \text{ h}^{-1}$  after 1 h under low power (5-10 W) MW irradiation. Moreover, the heterogeneous catalytic systems allowed their easy recovery and reuse, at least for three consecutive cycles, maintaining 89% of the initial activity and concomitant rather high selectivity.

*Keywords:* Mn<sup>II</sup>, Cu<sup>II</sup> and Ag<sup>I</sup> complexes; Arylhydrazones of active methylene compounds; Alcohol oxidation; Microwave-assisted oxidation; Catalyst recycling.

# RESUMO

Foram obtidos um novo monómero,  $[Mn(H_2O)_6][HL^{1a}]_2 \cdot 4H_2O$  (1), e um novo tetrâmero,  $[Cu(H_2O)Cu(H_2O)_4(\mu \cdot L^2)]_2 \cdot 2H_2O$  (2), por reacção de  $Mn(CH_3COO)_2 \cdot 4H_2O$  e  $Cu(NO_3)_2 \cdot 2.5H_2O$  com 2-(2-(dicianometileno)hidrazinil) benzenossulfonato (**NaHL**<sup>1</sup>) e 5-(2-(4,4-dimetil-2,6-dioxociclohexilideno)hidrazinil)-4-hidroxibenzeno-1,3-dissulfonato (**Na<sub>2</sub>H<sub>2</sub>L<sup>2</sup>**), respectivamente. A condensação de NaHL<sup>1</sup> com água em presença de acetato de manganês(II) tetra-hidratado conduziu a um novo ligando,  $HL^{1a} = 2-(SO_3^{-})-C_6H_4-(NH)N=C(C=N)[C(=O)(NH_2)]$ , resultante de ataque nucleófilo da água (a) a um grupo ciano de NaHL<sup>1</sup>. Estes complexos foram caracterizados por espectroscopia de IV, análise elementar e difracção de raios-X.

Foi encontrada uma nova reacção mediada por uma ligação de hidrogénio assistida por ressonância (RAHB) na interacção do 3-aminocrotononitrilo com o sal de diazónio do ácido 2-aminobenzenossulfónico em meio básico, que conduziu ao (*Z*)-2-(2-(1-ciano-2-oxopropilideno) hidrazinil)benzenossulfonato (**NaHL**<sup>3</sup>). Encontrou-se um novo método para a síntese de um complexo de Ag<sup>1</sup> com ligandos do tipo aril-hidrazona de compostos de metileno activos (AHMAC) exemplificado na reacção de nitrato de prata(I) com NaHL<sup>3</sup> em HNO<sub>3</sub>. Foram isolados dois novos complexos de cobre(II),  $[Cu(H_2O)_2(en)_2]^{2+}[(HL^3)^{-1}]_2$  (**3**) e  $[Cu(en)_2(\mu-L^3)^{2-}]_{2n}\cdot nH_2O$  (**5**), e um complexo de prata(I),  $[Ag_2(\mu-HL^3)_2]_n\cdot nH_2O$  (**4**), na reacção de NaHL<sup>3</sup> com Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O e AgNO<sub>3</sub> na presença de etilenodiamina (en) e HNO<sub>3</sub>, respectivamente. Todos estes complexos foram caracterizados por análise elementar, espectroscopia de IV e difracção de raios-X. A nuclearidade e organização supramolecular dos compostos obtidos dependeram do átomo metálico e das condições de reacção.

Os novos complexos (1-3) evidenciaram actividade catalítica elevada para a oxidação de alcoóis primários e secundários com hidroperóxido de *tert*-butilo assistida por microondas (MW) na presença de solventes e sem aditivos. Foram obtidos rendimentos dos produtos de oxidação até 85.5% e frequências de *turnover* (TOFs) até 1.90 x 10<sup>3</sup> h<sup>-1</sup> após 1 h de irradiação com MW de baixa potência (5-10 W). Acresce que a utilização de sistemas catalíticos heterogéneos permitiu a sua fácil recuperação e reutilização, pelo menos durante três ciclos consecutivos e mantendo 89% da actividade inicial e a concomitante elevada selectividade.

**Palavras-chave:** Complexos de Mn<sup>II</sup>, Cu<sup>II</sup> and Ag<sup>I</sup>; Aril-hidrazonas de compostos de metileno activos; Oxidação de alcoóis; Oxidação assistida por microondas; Reciclagem de catalisadores.

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# **ABBREVIATION LIST**

In this thesis has been used the following abbreviation:

- AACs Aromatic azocompounds
- ADBs Azo derivatives of  $\beta$ -diketones
- AHBDs Arylhydrazones of β-diketones
- AHMs Arylhydrazone of malononitrile
- AHMACs Arylhydrazones of methylene-active compounds
- DMSO Dimethylsulfoxide
- GS Gas cromatografy
- en Ethylendiamine
- IR Infrared
- MACs Methylene-active compounds
- MeOH Methanol
- NaHL<sup>1</sup> sodium-2-(2-(dicyaninethylene)hydrazinyl)benzenesulfonate
- $Na_2H_2L^2 5,5$ -Dimethyl-2-(2-hydroxy-3,5-disulfophenylhydrazo)cyclohexane-1,3-dione
- NaHL<sup>3</sup>- sodium-2-(2-(1-cyano-2-oxopropylidene)hydrazinyl)benzenesulfonate
- NMR Nuclear magnetic resonance
- PZ Pyrazine
- RAHB Resonance assisted hydrogen bond
- SAHAMCs Sulfo-functionalized arylhydrazones of active methylene compounds
- SAHBDs Sulfo arylhydrazone of  $\beta$ -diketones TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl
- TBHP Terz-butylhydroperoxide
- TEMPO 2,2,6,6-tetramethylpiperidyl-1-oxyl
- TGA Thermogravimetric analysis
- TOF Turnover frequency
- TON Turnover number
- XRPD X-ray powder diffraction

# **1. INTRODUCTION**

# 1.1 Aromatic azocompounds (AACs)

Aromatic diazo compounds (Figure 1.1) was discovered by Peter Griess (1828-1886), in 1858. He chose the name "diazo" because he thought that two hydrogen atoms of benzene can be replaced by two nitrogen atoms, in reality it is not so. Aromatic azocompounds (AACs) are very important class of compounds in organic chemistry because they are widely used in organic chemistry like dyes, indicators, pigments, food additives, radical reaction initiators, therapeutic agents, etc.<sup>(1,2)</sup>. This type of compounds containing one or more of -N=N- group that are called "azo" group in the molecular structure which form bridges between two organic residue, of which at least one is usually an aromatic nucleus<sup>(3)</sup> (Figure 1.1) where one of the R group are aromatic.



Fig. 1.1: General structure of an aromatic azocompound.

There are a lot of methods to prepare these types of compounds, in particular, their discoverer *Griess*, in the 1858, reported in his work the diazotization of ortho-aminophenol **1** with nitrous acid (which itself was generated in situ by the reduction of nitric acid with arsenous acid) to afford the diazo-compound **2**. After considerable investigation the correct structure of **2** was finally deduced in which the  $-NH_2$  group had been replaced by  $-N_2$  (Scheme 1.1)<sup>(1,2)</sup>.



Scheme 1.1: Preparation of diazonitrophenol 2 according to Griess.

At the present time, this method is not large used because there are a lot of more convenient ways to obtained the diazonium salt, for example, after Griess, Emil Knoevenagel (1865-1921) a German chemist, modified the Griess's original method for diazotization, he replacing the nitrous acid gases by the more accurately controllable alkyl nitrites as the source of nitrous acid. He found that nitrite esters were equally effective in this transformation, as illustrated in the preparation of **5** from **3** in acidic media (Scheme 1.2).<sup>(4,5)</sup>.



Scheme 1.2: Preparation of diazonium compound using Knoevenagel's method.

We can schematize the dominant reaction (diazotization reaction) for the preparation of diazo compounds in the following general manner (Scheme1.3):

 $ArNH_2 + HX + HNO_2 - RrN_2X + 2H_2O$ 

Scheme 1.3: General diazotization reaction.

where Ar is an aromatic radical which may be substituted and HX is a strong acid<sup>(6)</sup>.

Griess and Knoevenagel, were therefore the first to work on diazo compounds and thanks to them, a large number of chemists began to work in this direction trying to modify and optimize the method of preparation of diazo compounds. In fact, a number of modified procedures have been developed for syntheses of diazo-compounds.

*Direct methods.*<sup>(6)</sup> involve the use of metallic nitrite that is added in the solution of strongly basic amines in aqueous mineral acids (Scheme 1.4). The use of this method is limited to the basicity of the

arylamine because because at least a proportion of the amine present must be in solution as salt in the aqueous acid, since the nitrous acid reacts only with the dissolved amine. So, the basicity of the arylamine must be sufficient. Martius<sup>(7)</sup> was the chemist that introduced sodium nitrite as the source of nitrous acid. The liberation of nitrous acid by the action of mineral acid and its attack on the arylamine salt occur with great rapidity.

 $ArNH_2 + NaNO_2 + 2HX$   $\rightarrow ArN_2X + NaX + 2H_2O$ 

Scheme 1.4: Direct methods to formation of diazonium compound.

These reaction take place with liberation of heat that could prevent its speed as it is difficult to eliminate all the heat liberated to prevent any increase in temperature. A good choose is to conduct the reaction in ice bath. In general two equivalent of acid is the theoretical amount necessary to conduct the reaction but probably is not enough because there is always the risk of diazoamino-compounds that can appear if the solution are not sufficiently acid until completion of the reaction.

*Inverted method:* consist in the treatment with excess of cold mineral acid of an alkaline solution of metallic nitrite and salt of sulphonated or carboxylated aryl amines<sup>(6)</sup> (Scheme 1.5).



Scheme 1.5: General scheme.

The solutions of sodium sulphanalate and sodium nitrite in water are added into dilute solution of sulphuric acid with stirring, diazocompound was precipitated out (Scheme 1.6).



Scheme 1.6: Diazotization of sulphanilic acid.

*Witt method*<sup>(8)</sup>: this method is based on the using of concentrated nitric acid as solvent for the amine and a reducing agent at the same time to produce the nitrous acid necessary for the diazotization<sup>(8)</sup>.

This procedure start using a solution of aryl amine in nitric acid, at this solution was added metabisulphite. In particular, dinitrotoluidine, was was treated with sodium metabisulphite and then

nitric acid was added in the mixture at 0 °C to obtain the diazonium compound in quantitative yield (Scheme 1.7). The method is not suitable for technical purposes, but it is sometimes useful for experimental purposes.



Scheme 1.7: Diazotisation of 3,5-dinitro-o-toluidine.

*General method:* includes, oxidation reaction<sup>(6)</sup> (this reaction are carried out in presence of oxidizing agents like mercuric oxide<sup>(8)</sup>, mercuric acetate<sup>(9)</sup>, bromine<sup>(10)</sup>, nitrous acid<sup>(11)</sup>, nitrogen trioxide<sup>(12)</sup>; reduction reaction<sup>(6)</sup> (nitrous acid<sup>(13)</sup>, hydroxylamine<sup>(14)</sup>, acetyl chloride<sup>(15)</sup> are reducing agents used to prepare diazo-compounds). The methods listed above are just some of the possible methodologies reported in the literature for the preparation of diazo-compounds.

In the last decades, the coordination chemistry of AACs has been extensively studied because of possible combination of interesting functional properties with a diversity of molecular geometries of their complexes. The interest of this complexes, involve a lot of different field like preparation of conducting and magnetic materials, non-linear optics materials, supramolecular chemistry, catalysis and bioinorganic chemistry, among others<sup>(1,2)</sup>.

### **1.2 Methylene-active compounds (MACs)**

Methylene-active compounds (MACs) (e.g.  $\beta$ -diketones,  $\beta$ -dinitriles, benzoylacetonitriles, cyanothioacetamide, ethyl cyanoacetate, cyanoanilides, etc.) are compounds that have a methylene group between two strong electron withdrawing groups, have also been of considerable interest in organic chemistry, for instance,  $\beta$ -diketones are important starting materials in many organic reactions<sup>(16, 17)</sup>. Many of MACs have been widely used in coordination chemistry for a long time and have recently been the object of increasing attention as constituents of polydentate ligands in metallo-supramolecular chemistry.

### 1.2.1 β-Diketones

 $\beta$ -diketones in particular, represent one of the oldest classes of chelating ligands. It was discovered that these particular compounds have properties as extracting and coordinating agents for the spectrophotometric determination of metal ions in dilute solutions, and for chromatographic

separations<sup>(18)</sup>. But these are not the only fields of application and research, another primary field of interest is the potential application of metal  $\beta$ -diketonates as liquid crystal phases<sup>(19,20)</sup>; catalytic features, in fact  $\beta$ -diketonates are important spectator donors for metal-intermediate species involved in several important organic reactions<sup>(21,22)</sup>; in the field of nanoscale materials,  $\beta$ -diketonate ligands play an important role as assembly agents in the preparation of high-spin molecules<sup>(23,24)</sup>.

Structure of  $\beta$ -diketones are very interesting because they exist as an equilibrium mixture of keto and enol tautomeric forms. Generally, the enol form are more stable than keto form due to intramolecular H-bonding and simultaneous conjugation (Scheme 1.8)<sup>(16)</sup>.



Scheme 1.8: Tautomeric equilibrium.

Obviously it can favor one or the other tautomeric form; the enolic form are favored in non-polar solvent; using electron withdrawing groups, we are able to shift the equilibrium to enol form and the reverse happens with electron-releasing substituents<sup>(16)</sup>.

There are several methods to can prepare  $\beta$ -diketones, the classical methods involve the Claisen condensation (Scheme 1.9), but with this procedure there are some problems like the formation of regioisomers, competing O-acylation, proton exchange between the enolate and the product diketone and poor yield.



Scheme 1.9: Claisen condensation.

In order to avoid the difficulties which could be encountered with Claisen condensations, chemists tried to found some new synthetic approaches. One of these are based on the C-acylation of metal (Li or Cu) enolates by acyl cyanides or chlorides (Scheme 1.10)<sup>(25)</sup>.



Scheme 1.10: Modification based on C-acylation of metal, M can be Li or Cu, X can be CN or Cl.

*New syntheses*, based on the condensation of  $\alpha$ -haloketones with acid chlorides or anhydrides catalyzed by Sml<sub>2</sub>, or C-acylation of enoxysilanes catalyzed by a mixture of BiCl<sub>3</sub>/Nal or BiCl<sub>3</sub>/Znl<sub>2</sub>, have been proposed (Scheme 1.11)<sup>(26)</sup>.



Scheme 1.11: New synthesis.

Another simple route to can obtained  $\beta$ -diketones is to heat the  $\alpha$ , $\beta$ -epoxyketones in the presence of tetrakis(triphenylphosphine) palladium(0) as catalyst and bis(diphenylphosphino)ethane (dppe) (Scheme 1.12)<sup>(27)</sup>.



**Scheme 1.12:** Heat to  $\alpha$ , $\beta$ -epoxyketones.

We cannot forget that we are able to prepare also chiral  $\beta$ -diketones that can be obtained by Claisen condensation also. However, the mentioned methods in that paragraph are some of the new route to synthesized  $\beta$ -diketones that are reported in literature.

 $\beta$ -diketones have been studied also in their ability to coordinate metals and was found that there are three principle mode to coordinate metals; diketones in the neutral form; diketonates in the mono- and dianionic forms<sup>(16)</sup>.

In neutral  $\beta$ -diketones, the most common example of coordination is O,O-bidentate keto form (I) and the less common O-monodentate keto form (II) (Figure 1.2).

About monoanionic  $\beta$ -diketonates, the most common mode of coordination are O,O-bidentate chelates (III), another is where one (IV) or more oxygen atoms (V) coordinate to other metal centers through a second lone pair (Figure 1.3).

About dianionic  $\beta$ -diketonates, interesting mode of coordination was found with metals like palladium (Pd) and platinum (Pt) or non-metallic elements. We can have (diketonates)<sup>2-</sup> like  $\eta^3$ -C<sub>3</sub>-tridentate to Pd through C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub>, in an allylic fashion (VI); in (VII), the donor is additionally O,O-bidentate chelating toward another metal (Figure 1.4). But in literature are reported more type of coordination mode about  $\beta$ -diketones, in this thesis I reported only the more important and common mode of coordination.



Fig. 1.2: Coordination mode of neutral β-diketones.



Fig. 1.3: Coordination mode of monoanionic β-diketonates.



Fig. 1.4: Coordination mode of dianionic  $\beta$ -diketonate.

Exist also, bi; tri and tetra  $\beta$ -diketones that are able to coordinate two atoms of the same metals or of different metals simultaneously, in a planar array<sup>(28)</sup>.

### 1.2.2 Malononitrile

The malononitrile are compounds having two cyano groups and they too are part of the class of compounds of MACs and have the general formuna  $CH_2(CN)_2$  (Figure 1.5). These compounds are very interesting as a starting materials in organic synthesis, in particular, malononitrile are useful to synthesized herbicides, dyes, polymers, washing and bleaching compositions, lubricants, optical sensitizers, etc<sup>(29)</sup>.



Fig.1.5: Structure of Malononitrile.

Malononitrile can form colorless crystals that are soluble in water. Both cyano groups, can undergo nucleophilic attack and more reaction. The malononitrile anion can formed by deprotonation using relative week bases<sup>(30)</sup>. The most important method to can prepare malononitrile until mid-1970, involve the dehydration of cynoacetamide using phosphorus pentachloride<sup>(31)</sup> or phosphorus oxychloride<sup>(32)</sup> in an inert solvent in a batch process (Scheme 1.13).



Scheme 1.13: Preparation of malononitrile.

Nowadays, this process are not so use, the main process are a continuous high-temperature process in which, acetonitrile and cyanogens chloride are fed into a tube reactor above  $700^{\circ}C^{(33)}$ .

# 1.3 Arylhydrazones of methylene-active compounds (AHMAC)

A combination of an AAC, in particular an arylhydrazone, with a MAC in one molecule (Figure 1.6) creates multifunctionalized arylhydrazones of methylene-active compounds (AHMACs). AHMACs are very interesting compounds because they are versatile starting materials for a number of organic syntheses: leading to compounds which are biologically active<sup>(34)</sup>, possess liquid crystal properties<sup>(35)</sup>, can be applied as analytical reagents<sup>(36)</sup>, indicators<sup>(37)</sup>, ionophores<sup>(38)</sup>, or hydrazone dyes<sup>(39)</sup>.



Fig. 1.6: Arylhydrazones of methylene-active compounds (AHMACs).

The first methylene-active arylhydrazones were reported as early as 1883, by Richter and Müntzer, then designated as "Benzolazoaceton"<sup>(40)</sup> which was five years later shown by Japp and Klingemann to be a hydrazone<sup>(41)</sup>. The synthesis of AHMACs consist in a coupling of a MAC with an aromatic diazonium salt, mostly performed in methanolic or ethanolic solution containing acetate<sup>(42)</sup> (Scheme 1.14).



Scheme 1.14: Japp-Klingemann synthesis of AHBD.

In particular, in the scheme show above the first step involve the conversion of aniline to produce the corresponding diazonium salt by diazotization with sodium nitrite in acidic medium<sup>(41,42)</sup>. The original procedure underwent many modifications and improvements, e.g. higher yields of more pure products can be obtained when the coupling is undertaken in a solution of sodium hydroxide instead of sodium acetate<sup>(38)</sup>. The acid used in the first step (diazotization), influence the yield and the stability of the diazonium salts<sup>(1,2)</sup>. The Japp-Klingemann method has given rise to an immense variety of AHMACs derived from various arylamines and MACs<sup>(34-38)</sup>. The AHMAC products are very interesting because they can be used as intermediates in further synthesis of organic molecules<sup>(34)</sup> or as a promising ligands in coordination chemistry.

Particular interest have the azo derivatives of  $\beta$ -diketones (ADBs), play a very important role in coordination chemistry because they are potentially versatile building blocks because containing both azo group and diketones group that give high potential in metal coordination<sup>(43)</sup>. The ADBs that have particular interest in metal coordination are the ones that containing functional groups like SO<sub>3</sub>, OH, Cl, NO<sub>2</sub> in *ortho* position, because when coordinate metal, they can form a polynuclear structure and the aryl group. These compounds are called Arylhydrazone of  $\beta$ -diketones (AHBDs).

AHBDs, exist in a tautomeric equilibrium<sup>(44)</sup> (Scheme 1.15), between the hydrazo and enol-azo form and this equilibrium are very important for the application of these compounds. In general, in the solid phase, AHBDs exist in the hydrazo form, in solution, are present in a mixture of both tautomers. The tautomeric transition are connected to the delocalization of  $\pi$  electrons "resonance assisted hydrogen bond" (RAHB).



Scheme 1.15: Tautomeric equilibrium between hydrazo and enol-azoform.

As already mentioned above, the AHBD with substituents in ortho position have particular importance in metal coordination also increase the stability of the complexes that are formed if we compare them to those of the simple AHBD<sup>(44,45)</sup> (scheme 1.16).



Scheme 1.16: Possible coordination mode of AHBDs (E=C, N, As, S).

AHBDs can exist in different tautomeric form, as already mentioned above, and isomers, (E/Z)-enolazo, keto-azo and (E/Z)-hydrazone (Scheme 1.15). The enol-azo form are favored in non-polar solvent, low temperature and solid state; the hydrazone form are favored when the temperature decreases, solvent polarity increase and when the substituent are electron-withdrawing; the keto-azo form have a very low stability compared to the other two form and are not detectable<sup>(46)</sup>. RAHB play a very important role, in fact in the solid phase AHBDs exist only in the hydrazone form with sixmembered ring that involve RAHB and =N-NH- and carbonyl group (Scheme 1.17).



Scheme 1.17: Possible tautomeric and isomeric form of AHBDs ortho substituted.

Other important compounds belonging to the class of AHMACs are arylhydrazone of malononitrile AHMs (Figure 1.7) a combination of aryl hydrazone and malonitrile.



Fig. 1.7: Arylhydrazone of malononitrile (AHMs).

As in the case of AHBDs, also AHMs can have an *ortho* substituent in the aromatic ring and this substitution becomes very important. In particular, the functional groups used are sulphonic group  $SO_3H$  and carboxylic group  $COOH^{(47)}$  (Figure 1.8).



Fig. 1.8: Sulfo arylidrazone of maloninitrile.

Also in the case of AHMs, the RAHB are important, in particular when there is an *ortho* substituent able to form intra-molecular hydrogen bonds, because these system can promote a nucleophilic attack and stabilized the product<sup>(48)</sup> (Figure 1.9).



Fig. 1.9: RAHB in AHMs with an ortho substituent.

The interesting thing is that the AHMs compounds are able to form a second RAHB chain with the nearest cyano group, in this way, the compound are "freezing" and the nucleophilic attack can happen only in the free cyano group<sup>(47)</sup> (Figure 1.10).



Fig. 1.10: Second RAHB in AHMs.

Even in the case of AHMs it is important to consider the possible E/Z isomers around the C=N bond in the hydrazone. The RAHB system are also important to favoured one isomer to another<sup>(48)</sup>.

# 1.3.1 Modification with SO<sub>3</sub>H group to form Sulfofunctionalized Arylhydrazone of Active Methylene Compuunds (SAHAMCs)

In literature was reported some modification of the simple structure of AHMACs ligand (Figure 1.2) to improve their coordination ability. For instance, it was observed that AHMACs containing a 2-hydroxyphenyl group can show a high complexing ability in solution<sup>(49)</sup>. The introduction of hydrophilic polar group like SO<sub>3</sub>H in *ortho* position in the aromatic ring of ligand AHMACs, give us a lot of advantages. The name of this type of ligand is Sulfo-functionalized Arylhydrazones of Active Methylene Compounds (SAHAMCs) (Figure 1.11).



Fig. 1.11: Sulfo-functionalized arylhydrazone of active methylene compounds (SAHAMCs).

With the introduction of sulfonic group, we are able to increase the solubility in water of the compounds and this is very important. The water solubility are particular important in catalysis and other application in which water is used as solvent and/or reactant<sup>(50)</sup>. The increases in solubility are not the only advantage that we can have introducing SO<sub>3</sub>H group, thanks to this group in *ortho* position, SAHAMCs are able to form the RAHB system that give, in particular to AHMs, a regioselective way for the nucleophilic attack on CN group<sup>(47)</sup>. The oxygen in the sulfonic group can form an hydrogen bond with the N=NH moiety.

Thanks to the sulfonic group in the proximity of the CN group in AHMs, the most advantage that we can have is the improvement in the ability of coordination of this compounds. In fact,  $SO_3H$  group have a good coordination ability and can facilitate the formation of the complexes with different structures<sup>(48)</sup>.

#### 1.4 Complexes of SAHAMCs

The interest in the coordination compounds of SAHAMCs as ligand, in recent years has increased and many of these coordination compounds are reported in literature<sup>(51)</sup>. In this thesis, I focus my attention in particular in the complexes with manganese (Mn<sup>II</sup>) copper (Cu<sup>II</sup>) and silver (Ag<sup>I</sup>) but in literature are reported also complexes that containing other metals like magnesium (Mg<sup>I</sup>), iron (Fe<sup>III</sup>), nickel (Ni<sup>II</sup>) and so on. The stability and reactivity of metal complexes are a function of both the position of the metal in the periodic table and the nature of the ligands<sup>(52)</sup>.

### 1.4.1 Complexes of metals with AHBDs

In solution the reactions of complex formation of metal ions with AHBDs proceed with a shift in the tautomeric equilibrium<sup>(49)</sup>. Generally the stabilities of metal complexes with AHBDs increase in the order  $Ca^{II} < Mg^{II} < Mn^{II} < Cd^{II} < Zn^{II} < Co^{II} < Ni^{II} < UO_2^{II} < Cu^{II} < Fe^{III}$ .

In literature are reported many different complexes using different metal, for instance, Na, Mg, Ru, Mn, Fe and so on and also with some lanthanide metals.

#### 1.4.1.1 Copper complexes

The AHBDs ligands, showed a very good ability to coordinate Cu<sup>II</sup>. Complexes of AHBDs with copper are found that are useful catalyst in particular for some oxidation processes, for example, the peroxidative oxidation reactions of cyclohexane and alcohol<sup>(50)</sup>.

The general mode to coordinate for Cu ion, are the chelating fashion creating a CuNNCCO metallacycle, while additional substituents may influence the overall geometry.

For instance, in the literature it is possible to find complex of 3-(arylhydrazone)pentane-2,4-diones with  $Cu^{II}$  salts that was isolated as a crystalline compounds resulting in a mononuclear complexes,

with ligand to metal ratio 2:1. The geometry of these complexes are square-planar and can formed 1Dchains thanks to the hydrogen bonds because contain water molecules<sup>(53)</sup> (Figure 1.12a).

Other study with this type of ligands were made by replacing of methyl group with a trifluoromethyl and in literature are reported that this exchange produce some different in the crystalline packing of complexes<sup>(54)</sup> (Figure 1.12b). In literature are also reported complexes in which the AHBDs ligands acts as a tetradentate ONO and O ligand in which, the central Cu are has the coordination number six, the terminal one has coordination number five (Figure 1.12c). This complexes are very important for the catalytic application<sup>(55)</sup>.

Another interesting way to synthesize the complexes containing Cu reported in the literature, involve the use of auxiliary ligands. Auxiliary ligands affect the coordination process trough coordination, template condensation or as a proton attractor or spacer, thus allowing the regulation of structures of the primary subunits as well as their supra-molecular assemblies<sup>(50)</sup>. For example, in literature are reported a Cu complexes of Sulfo arylhydrazone of  $\beta$ -diketones (SAHBDs) synthesized in the presence of pyrazine (pz) gives rise to the 1D coordination polymer<sup>(56)</sup>. Central Cu showed a distorted octahedral coordination, being connected via oxygen atoms of the sulfa groups. Hydrogen bonds involving the uncoordinated carbonyl group, coordinated water and pz molecules give rise to the stack formation of a supramolecular 3D associate (Figure 1.12d).

The substituents in the  $\beta$ -diketone fragment and in *ortho* position on the aromatic part of the AHBDs ligands strongly influence the overall structures of the complexes. In fact, some complexes reported in literature are dimmers, some are monomers and some are polymers associated by intense  $\pi$ ·· $\pi$  interactions involving metallacycle rings. Are also possible found some binuclear complexes (Figure 1.11e).



Fig. 1.12: Some of the Cu<sup>II</sup> complexes with AHBDs reported in literature.

### 1.4.1.2 Magnesium complexes

Complex found with this type of metal is a salt, in wich ligand stay out of the coordination sfere of metal<sup>(55)</sup> (Fig. 1.13). The magnesium coordination number is 6 and its positive charge is neutralized by the deprotonated carboxyl groups and hydroxyl ligands. The MgII ions are combined through hydroxyand aqua-bridges in 1D chain, while the RAHB system is preserved within the AHBD ligand.



Fig. 1.13: Magnesium complex

### 1.4.1.3 Iron complexes

Complex found with Iron(III) were isolated in solid state upon reaction of  $Fe^{III}$  chloride with respectively ligand in acidic medium (pH 2)<sup>(55)</sup> (figure 1.14).Both octahedral type structures are similar, with the effective charge of  $Fe^{III}$  being neutralized by the deprotonated sulfo group, alkoxy oxygen atoms and hydrazone nitrogen.



Fig.1.14: Iron complexes

### 1.4.1.4 Nichel complexes

One of the complexes found using nichel(II) as metal, is mononuclear and bears two six-membered chelate metallacycles involving a nearly regular  $N_2O_2$  square planar coordination geometry<sup>(55)</sup>. In the crystal packing, strong and weak H-bond interactions lead to a supramolecular network structure (figure 1.15). Other complexes for example are monomers (figure 1.16).



Fig.1.15: Mononuclear complex



Fig.1.16: Monomer complexes

### 1.4.2 Complexes of metals with AHMs

Using the ligands AHMs, we must take into account that nucleophilic attack at CN group can happen because the complexes formation occurs in solution. In fact, in the presence of methanol, ethanol, water, ethylamine and ethylenediamine, nucleophilic attacks to the cyano moieties occur leading to a variety of ligated amidines, carboxamides and iminoesters depending on the starting ligands, nucleophiles and conditions used.

### 1.4.2.1 Copper complexes

As in the case of AHBDs complexes, in literature are reported monomeric, tetranuclear and polymeric complexes of AHMs<sup>(48)</sup> (Figure 1.17 a, b, c). The nuclearity and type of structure of the formed complexes depend on AHM, the nucleophile and conditions (solvents, temperature, and time) used for the synthesis. In general, only one of the two CN groups undergoes nucleophilic attack, this is why upon coordination to Cu<sup>II</sup> the product of one nucleophilic are stabilized<sup>(48)</sup>. In this case, Cu atom can have square-pyramidal coordination environments or octahedral coordination environment. These complexes form easy hydrogen bond. The mode of coordination involve one N-hydrazone atom, a sulfonyl oxygen atom and an additional N- or O atom from the organic ligand, leading to two fused sixmembered rings. Some complexes reported an extra five-membered metallacycle, some a four-membered metallacycle due to the central Cu<sub>2</sub>O<sub>2</sub> cores (Figure 1.17 d, b).



**Fig. 1.17:** Some of the Cu<sup>II</sup> complexes with AHMs reported in literature.

#### 1.4.2.2 Manganese complexes

In literature are also reported some manganese II and III complexes of AHMs<sup>(55)</sup>.

The template one-pot transformations of an AHM ligand and manganese II, give three different complexes with different nuclearity (Figure 1.18 a). In literature are also reported the first example of a tetradecanuclear Mn<sup>II</sup> aggregate (figure 1.18 b) in which the antiferromagnetic coupling dominate.

Are also reported one mononuclear hexa-coordinate complex that show multiple intramolecular RAHB systems stabilize the molecule (Figure 1.18 c)



Fig. 1.18: Some of the manganese complexes with AHMs reported in literature.

### **1.5 Catalytic Application of complexes**

The main application of Cu complexes of SAHAMCs are in catalysis. Particular interest was focused on copper and this is why the chemistry of copper is extremely rich because it can easily access Cu<sup>0</sup>, Cu<sup>II</sup>, Cu<sup>III</sup>, and Cu<sup>III</sup> oxidation states allowing it to act through one-electron or two-electron processes. The different oxidation number of copper are easily associated with a large number of functional groups. These properties, allowing copper to catalyzed the oxidation reactions<sup>(57)</sup>.

One of the most important reaction in organic chemistry, is the oxidation of primary and secondary alcohols to carbonyl compounds (Scheme 1.18-1.19). This type of reaction are very efficient using a large number of oxidant agent, but the problem is that these oxidant are not so green and harmful like CrO<sub>3</sub> or KMnO<sup>4</sup>, and/or halogenated solvents, that results in the generation of large amounts of waste. Chemist are interested in finding catalytic procedure to perform the oxidation reaction using green oxidant<sup>(58)</sup>. It is known that microwave irradiation (MW) can provide a much more efficient synthetic

method than conventional heating, so that similar yields can be obtained in a shorter time and/or the selectivity can be improved <sup>(59,60)</sup>. It also important use a green solvent in this type of reaction and so, the develop of water soluble water-soluble catalysts with pH-tunable sites is of interest for novel green catalytic processes and recycling systems<sup>(61)</sup>. As mentioned in paragraph 1.3.1, sulfonic group are perfect for this purpose.



Scheme 1.18: MW-assisted oxidation of 1-phenylethanol to acetophenone.



Scheme 1.19: MW-assisted oxidation of phenylmethanol to benzaldehyde.

The catalytic activity of different copper complexes of SAHAMCs was reported in literature for the oxidation of benzylic alcohol substituted and not resulting in a good catalytic activity and selective oxidation<sup>(62)</sup>. Oxidation of alcohol are not the only oxidation reaction to can test the catalytic activity of these type of complexes.

In literature are reported the catalytic activity of Cu<sup>II</sup>–AHBDs complexes in the peroxidative oxidation of cyclohexane<sup>(63)</sup> for instance (Scheme 1.20).



Scheme 1.20: Peroxidative oxidation of cyclohexane.

Oxidation of alcohol or hydrocarbons are not the only reaction reported in literature catalysed from copper complexes. Epoxidation of hydrocarbons, alkyl, aryl, and alkenyl anion coupling, reactions of enamines and enol ethers, reactions of phenols and naphthols, reactions of anilines, reactions of

amines, reactions of azides, reactions of ethers are the main class of reaction reported in literature in which, copper complexes are successful used<sup>(57)</sup>.

## 2. AIM OF THE THESIS

The aim of this Masters thesis concerns the synthesis of sulfo-functionalized arylhydrazones of active methylene compounds (SAHAMCs) and their use as starting materials for the generation of new supramolecular and coordination compounds namely of Ag(I), Mn(II) and Cu(II), the latter for application in catalysis.

SAHAMCs are of particular interest because they possess a rich coordination chemistry, can form two- or three-centred resonance-assisted hydrogen bonds depending on the position of the  $-SO_3^-$  group, and are easy to handle owing to their stability and high solubility in polar solvents. Furthermore, their basic form is readily obtained in view of the easy deprotonation of the sulfonic group ( $-SO_3H$ ) in the acidic form. This can allow a reversible tuning of the acid-base properties of the catalyst, what can enhance the activity/selectivity. Thus, the work is expected to constitute to the synthesis of aqua-soluble complexes with pH-tunable sites for protonation-deprotonation. The Cu<sup>II</sup>-SAHAMCs complexes will be tested as catalyst precursors for the selective oxidation of alcohols to the corresponding carbonyl compounds.

### **3. EXPERIMENTAL**

### 3.1 Reagents

Chemicals using in this work were obtained from commercial sources (Aldrich).

Sodium Hydroxide NaOH  $\geq$  98%; Sodium Nitrate NaNO<sub>3</sub>  $\geq$  99%; Hydroclhoridric acid HCI; Sodium acetate anhydrous CH<sub>3</sub>COONa  $\geq$  99%; Copper Nitrate Cu(NO<sub>3</sub>)<sub>2</sub> \* 4H<sub>2</sub>O  $\geq$  99%; Manganese acetate Mn(CH<sub>3</sub>COO)<sub>2</sub>; Silver Nitrate (AgNO<sub>3</sub>), Nitric acid (HNO<sub>3</sub>) Ethanol CH<sub>3</sub>CH<sub>2</sub>OH; 2-hydroxy-3,5-disulfoaniline; 2-aminobenzenesulfonic acid; 3-Aminocrotononitrile C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>; Water H<sub>2</sub>O; Acetone (CH<sub>3</sub>)<sub>2</sub>CO; Methanol CH<sub>3</sub>OH; 1-phenylethanol; tert-butyl hydroperoxide TBHP; acetonitrile CH<sub>3</sub>CN; Benzaldehyde C<sub>6</sub>H<sub>5</sub>CHO.

# 3.2 Techniques and apparatus

#### 3.2.1. X-Ray single crystal diffraction

X-Ray diffraction is one of the most powerful techniques for the determination of 3D structure of crystalline compound. With this technique, we are able to understand relative position of the atoms, bond lengths and angles, torsion angles, conformation and flexibility of the molecule. Allows us the understanding of the non-bonded interactions (*e.g.*, H-bond interactions) and therefore the 3D arrangement. Quite frequently, this technique is non-destructive. The radiation are obtained when electrons produced by termoionic emission from a W filament are accelerated by potential difference towards the anode.

Von Laue discovered X-ray interference at crystal lattices and proved the wave nature of X-rays in 1912 together with Walther Friedrich and Paul Knipping. A simple way to describe the diffraction conditions established by L. Bragg in 1912, is to consider the diffraction as a reflection of the X radiation by adjacent planes in the crystal lattice  $n\lambda = 2d \sin\theta$  (Figure 3.1). Diffraction occurs when a X-ray (with  $\lambda$  wavelength) focus into the set of parallel planes (with d distance) with  $\theta$  angle and is reflected at the same angle.


Fig. 3.1: Representation of Brag's law.

What happens when the X-Ray impact with the crystals?

When the X-ray beam hits a crystal, all the atoms in the crystal disperse the radiation in all the directions. In most cases, the radiation is cancelled (destructive interference), but in certain direction it is added (constructive interference) and forms a diffracted beam. Different planes disperse the radiation in such a way that each diffracted beam can be visualized as a reflection of the incident beam by a system of parallel planes separated by a distance *d*. A detector registers the position and intensity of each beam. A computer registers the position, intensity and orientation of the crystal for each reflection. Crystals produce  $10^2 - 10^5$  reflections. Each crystal produces a unique pattern of reflections, as a finger print. The interpretation of the pattern leads to the crystalline and molecular structure (Figure 3.2).



Fig. 3.2: X-Ray diffraction.

Quality crystals were immersed in cryo-oil, mounted in a Nylon loop (Figure 3.3 b) and measured at ambient temperature. Intensity data were collected using a Bruker AXS-KAPPA APEX II PHOTON 100 diffractometer with graphite monochromated Mo-K $\alpha$  (0.71073 Å) radiation (Figure 3.3 a).



Fig. 3.3: a) Core of the machine, b) loop.



Fig. 3.4: Diffraction pattern.

#### 3.2.2. X-Ray powder diffraction

X-ray powder diffraction (XRPD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analysed material is finely ground, homogenized, and average bulk composition is determined. X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). Determination of unknown solids is critical to studies in geology, environmental science, material science, engineering and biology.

X-ray diffractometers consist of three basic elements: an X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced.

X-ray powder diffraction patterns (XRPD) were recorded in the reflection mode using a D-8 Bruker AXS diffractometer operating at 40 kV and 40 mA, using CuK $\alpha$  radiation ( $\lambda$  = 1.5418 Å). The XRD patterns were collected at 20 values ranging from 3° to 70° with step 0.02°.

#### 3.2.3. IR

Infrared Spectroscopy is the analysis of infrared light interacting with a molecule. The main use of this technique is in organic and inorganic chemistry. It is used by chemists to determine functional groups in molecules. IR Spectroscopy measures the vibrations of atoms, and based on this it is possible to determine the functional groups. Generally, stronger bonds and light atoms will vibrate at a high stretching frequency (wavenumber).

The components of an IR machine are the IR source, beam splitter, monochromator, a transducer, an analog to digital converter and a digital machine to quantify the readout.

Infrared spectra (4000 – 400 cm<sup>-1</sup>) of ligand and crystals were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets.

### 3.2.4. Mass Spectrometry

Mass spectrometry is an analytic technique used to identify the amount and type of chemicals present in a sample by measuring the mass-to-charge ratio. In general this technique is coupled with other separating technique for example gas-comatrografy.

In a general MS procedure, a sample is ionized, this may cause some of the sample's molecules to break into charged fragments. Iones are then separate according to their mass-to-charge ratio, now, a detector revels these mass-to-charge ratio.

Electrospray mass spectra were carried out with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. The solutions in methanol were

continuously introduced into the mass spectrometer source with a syringe pump at a flow rate of 10  $\mu$ L/min. The drying gas temperature was maintained at 350 °C and dinitrogen was used as nebulizer gas at a pressure of 35 psi. Scanning was performed from *m*/*z* = 50 to 1000.

### 3.2.5. Elemental Analysis

Elemental analysis is an experiment that determines the amount (typically a weight percent) of an element in a compound. The most common type of elemental analysis is for carbon, hydrogen and nitrogen, CHN analysis, is accomplished by combustion analysis. A sample is burned in an excess of oxygen and various trap, collecting the combustion products: carbon dioxide, water and nitric oxide. The mass of these combustion products can be used to calculate the composition of unknown sample. This type of analysis is especially useful for organic compounds.

Carbon, hydrogen, and nitrogen elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico in Lisbon, Portugal.

#### 3.2.6. Thermal Analysis

Thermal analysis is a physical chemical methods which deal with studying materials and processes under conditions of programmed changing's of the surrounding temperature. For this study was used thermogravimetric analysis (TGA), this technique can provide information about physical phenomena, such as second-order phase transition, including vaporization, sublimation, absorption, adsorption, and desorption. Likewise, TGA, can provide information about chemical phenomena including chemisorption, desolvatation, decomposition and solid-gas reactions.

Thermal properties were analysed with a Perkin-Elmer Instruction system (STA6000) at a heating rate of 10 K·min<sup>-1</sup> under air.

#### 3.2.7. NMR

NMR is a technique used to determine a compound's unique structure. It identifies the carbonhydrogen frameworks of an organic compound. The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged. If an external magnetic fields applied, an energy transfer is possible between the base energy to a higher energy level. The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency. The signal that matches this transfer is measured in many ways and processed in order to yield an NMR spectrum for the nucleus concerned.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at room temperature on a Bruker Avance II + 300 (UltraShieldTM Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference.

Coupling constants are in Hz; abbreviations: s, singlet; d, doublet; m, complex multiplet; vt, virtual triplet; br, broad.

#### 3.2.8. UV-visible

UV-visible spectroscopy is a technique used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopy analysis is commonly carried out in solutions but solids and gases may also be studied. The base of this technique is that molecules that contains  $\pi$ -electrons or non-bonding electrons can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons, the longer the wavelength of light it can absorb.

The final result is an absorption spectra.

The UV-vis absorption spectra in the 200 – 700 nm region were recorded with a scan rate of 240 nm·min<sup>-1</sup> by using a Lambda 35 UV-vis spectrophotometer (Perkin-Elmer) in 1.00 cm quartz cells at room temperature, with a concentration of compounds of  $1.00 \cdot 10^{-5}$  M.

#### 3.2.9. Catalysis

The catalytic tests under microwave irradiation (MW) were performed in a focused Anton Paar Monowave 300 microwave reactor using a 10 mL capacity reaction tube with a 13 mm internal diameter, fitted with a rotational system and an IR temperature detector.

Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm) and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. The initial temperature was maintained at 140 °C for 1 min, then raised 10 °C/min to 220 °C and held at this temperature for 1 min. Helium was used as the carrier gas.

# 3.3 Procedure

## 3.3.1. Synthesis of ligand NaHL<sup>1</sup>

The compound NaHL<sup>1</sup> (Figure 3.5) was synthesized via the Japp-Klingemann reaction between 2sulfophenyldiazonium chloride and malononitrile in an ethanolic solution containing sodium acetate.

#### Diazotization

2-aminobenzenesulfonic acid (3.46 g, 20 mmol) was dissolved in 50 mL water, and (0.80 g, 20 mmol) of NaOH was added. The solution was cooled in an ice bath to 273 K and 1.38 g (20 mmol) of NaNO<sub>2</sub> was added; 4.00 mL HCl were then added in 0.5 mL portions for 1 h. The temperature of the mixture should not exceed 278 K.

#### **Azo Coupling**

 $CH_3COONa$  (4.10 g, 50 mmol) was added to a mixture of 1.32 g (20 mmol) of malononitrile with 50 mL of ethanol. The solution was cooled in an ice bath to *ca.* 273 K, and a suspension of 2-sulfophenyldiazonium chloride (see above) was added in three portions under vigorous stirring for 1 h. The formed yellow precipitate of ligand was filtered off, washed with acetone and dried in air.

Yield 90 % (based on malononitrile), yellow powder soluble in methanol, ethanol, water. Anal. Calcd for C<sub>9</sub>H<sub>6</sub>N<sub>4</sub>NaO<sub>3</sub>S (M = 272.22): C, 39.71; H, 1.85; N, 20.58. Found: C, 39.49; H, 2.10; N, 20.23. MS (ESI): m/z: 251 [M+H]<sup>+</sup>. IR (KBr, selected bands, cm<sup>-1</sup>): 3099 v(NH), 2218 and 2227 v(C=N) and 1587 v(C=N). 1H NMR (300.13 MHz, DMSO-d6),  $\delta$ : 7.09–7.93 (4H, Ar–H), 13.33 (<sup>1</sup>H, NH). <sup>13</sup>C{<sup>1</sup>H} NMR (75.468 MHz, DMSO-d6), 87.2 (C=N), 109.0 (CN), 113.6 (C=N), 115.5, 125.3, 127.7 and 131.0 (Ar–H), 134.1 (Ar–SO<sub>3</sub>Na), 136.0 (Ar–NH–N).



Fig.3.5: New ligand NaHL<sup>1</sup>

## 3.3.1.1 Manganese Complex synthesis 1

Manganese acetate tetrahydrate  $Mn(CH_3COO)_2 \cdot 4H_2O$  (0.245 g, 1 mmol) was added to a solution of NaHL<sup>1</sup> (0.272 g, 1 mmol) in acetone-water (3:1, v/v) mixture (30 mL). The reaction mixture was heated under reflux for 3 h, there was a deep red precipitate. The reaction mixture was filtered, the filtrate was rejected. The residue obtained was washed several times with acetone. The crystals of

 $[Mn(H_2O)_6][HL^{1a}]_2 \cdot 4H_2O$  (1)  $(HL^{1a} = 2 \cdot (SO_3^{-}) - C_6H_4 - (NH)N = C(C \equiv N)[C(=O)(NH_2)])$  suitable for X-ray structural analysis were obtained by slow evaporation of a methanol solution of the deep red solid.

Yield, 70 % (based on Mn). Anal. Calcd. for  $C_{18}H_{34}MnN_8O_{18}S_2$  (M = 769.61): C, 28.09; H, 4.45; N, 14.56. Found: C, 28.42; H, 4.61; N, 14.17 %. MS (ESI): m/z: 163.0 [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> and 269.1 [(H<sub>2</sub>L<sup>1a</sup>)+H<sup>+</sup>]. IR, cm<sup>-1</sup>: 3515 v(OH), 3103 v(NH), 2230 v(C=N), 1697 v(C=O), 1589 v(C=N).



Fig.3.6: New manganese complex 1.



Scheme 3.1: Nucleophilic attack of water on a cyano group.

# 3.3.2. Synthesis of ligand Na<sub>2</sub>H<sub>2</sub>L<sup>2</sup>

The compound  $Na_2H_2L^2$  (Figure 3.7) was synthesized via the Japp-Klingemann reaction (Japp and Klingemann 1888) between the respective aromatic diazonium salt and pentane-2,4-dione in an ethanolic solution containing sodium acetate.

#### Diazotization

A 6.7250 g (0.0250 mol) portion of 2-hydroxy-3,5-disulfoaniline was dissolved in 50.00 mL of water while gently heating upon addition of 1.00 g of crystalline NaOH. Then, the solution was cooled down on an ice bath to 0°C and 1.7250 g (0.0250 mol) NaNO<sub>2</sub> was added, where after 5.00 mL 33% HCl was added in portions for 40 min. The temperature of the mixture should not exceed +5°C. A suspension of the unstable 2-hydroxy-3,5-disulfobenzodiazonium chloride  $[N=N{CC(OH)C(SO_3H)CHC(SO_3H)CH}]^+CI^-$  was obtained (Japp and Klingemann 1888) which then was used as such for the next stage (see as follows).

#### **Azo Coupling**

An amount of 5.00 g CH<sub>3</sub>COONa were added to a mixture of 3.50 g (0.025 mol) of 5,5dimethylcyclohexane-1,3-dione with 25.0 mL of ethanol. The solution was cooled on an ice bath, and a suspension of 2-hydroxy-3,5-disulfobenzodiazonium chloride was added in portions. In the azo coupling, the pH should be maintained in the range of 8–10; crystalline CH<sub>3</sub>COONa must be added if needed. On the next day, the precipitated reagent was filtered off, washed with ethanol, and dried in air. The formation of only one compound in the synthesis was confirmed by paper chromatography; the identity of the new obtained compound as sodium 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene) hydrazinyl)-4-hydroxybenzene-1,3-disulfonate ( $Na_2H_2L^2$ ) was demonstrated by elemental analysis, IR and <sup>1</sup>H, and <sup>13</sup>C NMR spectrometry.

Yield 74.00% (based on 5,5-dimethylcyclohexane-1,3-dione), red brown powder, soluble in water, DMSO, methanol, and insoluble in chloroform. Anal. Calcd for  $C_{14}H_{14}Na_2N_2O_9S_2$  (M = 464.38): C, 36.21; H, 3.04; N, 6.03. Found: C, 36.06; H, 3.08; N, 6.01%. IR, cm<sup>-1</sup>: 3447 v(OH), 2957 v (NH), 1648 v (C=O), 1590 v (C=O<sup>...</sup>H), 1561 v (C=N), 779 v (Ar). <sup>1</sup>H NMR (DMSO):  $\delta$  = 0.96 (s, 3H, CH<sub>3</sub>), 1.27 (s, 3H, CH<sub>3</sub>), 2.48 (s, 2H, CH<sub>2</sub>), 2.48 (s, 2H, CH<sub>2</sub>), 7.69–7.71 (s, 2H, Ar-H), 11.73 (s, 1H, OH), 14.17 (s, 1H, NH). <sup>13</sup>C{<sup>1</sup>H} (DMSO):  $\delta$  = 28.12 (CH<sub>3</sub>), 30.69 (CH<sub>3</sub>), 51.86 (2CH<sub>2</sub>), 114.30 (Ar-H), 114.54 (Ar-H), 125.34 (Ar-SO<sub>3</sub>Na), 124.60 (Ar-SO<sub>3</sub>Na), 128.40 (Ar-OH), 133.47 (Ar-NH-N), 175.60 (C=N), 206.58 (C=O), 206.90 (C=O).



Fig.3.7: New ligand  $Na_2H_2L^2$ .

## 3.3.2.1 Copper Complex synthesis 2

Copper tetramer,  $[Cu(H_2O)Cu(H_2O)_4(\mu-L^2)]_2 \cdot 2H_2O$  (2), was obtained after reaction of  $Cu(NO_3)_2 \cdot 2.5H_2O$  with sodium 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-4-hydroxybenzene-1,3-disulfonate  $(Na_2H_2L^2)$ . Thus, copper nitrate  $Cu(NO_3)_2 \cdot 2.5H_2O$  (0.37 g, 2 mmol) was added to a solution of  $Na_2H_2L^2$  (0.42 g, 1 mmol) in MeOH/water (2:1 v/v) mixture (30 mL). The reaction mixture was evaporated slowly at room temperature to favoured the formation of crystals. After two days, greenish–black crystals appears.

Yield, 75% (based on Cu). Anal. Calcd. for  $C_{28}H_{46}Cu_4N_4O_{29}S_4$  (M = 1285,12) C, 26.17; H, 3.61; N, 4.36. Found: C, 20.51; H, 3.005; N, 5.87. IR, cm<sup>-1</sup>: 1637 v(C=O), 1589 v(C=O), 1498 v(C=N).



Fig.3.8: New copper complex 2.

## 3.3.3 Synthesis of ligand NaHL<sup>3</sup>

The compound NaHL<sup>3</sup> (Figure 3.9) was synthesized via the Japp-Klingemann reaction (Japp and Klingemann 1888) between the respective aromatic diazonium salt and 3-aminocrotononitrile in an ethanol solution containing sodium hydroxide.

#### Diazotization

2-aminobenzenesulfonic acid (3.46 g, 20 mmol) was dissolved in 50 mL water, and (0.80 g, 20 mmol) of NaOH was added. The solution was cooled in an ice bath to 273 K and 1.38 g (20 mmol) of NaNO<sub>2</sub> was added; 4.00 mL HCI were then added in 0.5 mL portions for 1 h. The temperature of the mixture should not exceed 278 K.

#### **Azo Coupling**

1.64 g (20 mmol) of 3-aminocrotononitrile was dissolved in 30 mL of methanol. A solution of sodium hydroxide was added to a methanol solution containing 3-aminocrotononitrile. Than, this solution was added to the solution of diazonium salts under vigorous stirring. The solution was cooled in an ice bath to *ca.* 273 K. A orange precipitate appear and after 3h, the solution was filtered and precitate collect.

Yield, (based on) orange powder soluble in water, DMSO, methanol. The identity of the new obtained compound sodium (*Z*)-2-(2-(1-cyano-2-oxopropylidene)hydrazinyl) benzenesulfonate (**NaHL**<sup>3</sup>) was confirmed by elemental analysis, IR and <sup>1</sup>H, and <sup>13</sup>C NMR spectrometry. Anal. Calcd for C<sub>10</sub>H<sub>8</sub>N<sub>3</sub>NaO<sub>4</sub>S (M = 289.24): C, 41.52; H, 2.79; N, 14.53. Found: C, 41.32; H, 3.02; N, 14.23. IR, cm<sup>-1</sup>: 3459 v(OH), 2361 v (NH), 2206 v(C=N), 1645 v (C=O), 1534 v (C=O<sup>---</sup>H), 1453 v (C=N), 802 v (Ar). <sup>1</sup>H NMR of a mixture of isomeric *E*- and *Z*-hydrazone forms (300.130 MHz) in DMSO-*d*<sub>6</sub>, internal TMS, δ (ppm): *E*-Hydrazone, 2.84 (s, 3H, CH<sub>3</sub>), 7.15–7.69 (4H, Ar–H), 12.72 (s, 1H, N–H). *Z*-Hydrazone, 2.85 (s, 3H, CH<sub>3</sub>), 7.15–7.69 (4H, Ar–H), 14.04 (s, 1H, N–H). <sup>13</sup>C{<sup>1</sup>H} NMR (75.468 MHz, DMSO-*d*<sub>6</sub>). *E*-Hydrazone, δ: 52.65 (CH<sub>3</sub>), 104.81 (Ar–H), 110.69 (C=N), 115.12 (C=N), 116.15 (C=N), 124.26 (Ar–H), 127.48 (Ar–H), 130.42 (Ar–H), 134.01 (Ar–SO<sub>3</sub>Na), 136.72 (Ar–NHN=), 160.08 (C=O). *Z*-Hydrazone, δ: 52.75 (CH<sub>3</sub>), 105.66 (Ar–H), 115.24 (C=N), 116.15 (C=N), 124.61 (Ar–H), 127.66 (Ar–H), 130.70 (Ar–H), 135.11 (Ar–SO<sub>3</sub>Na), 137.43 (Ar–NHN=), 160.98 (C=O).



Fig. 3.9: New ligand NaHL<sup>3</sup>.

## 3.3.3.1 Copper Complex synthesis 3

Copper nitrate  $Cu(NO_3)_2 \cdot 2.5H_2O$  (0.37 g, 2 mmol) and 0.1 mL of ethylendiamine was added to a solution of NaHL<sup>3</sup> (0.29 g, 1 mmol) in MeOH-water-acetone (2:1:2 v/v) mixture (30 mL). The reaction mixture was evaporated slowly at room temperature to favoured the formation of crystals. After one day, greenish–black crystals of  $[Cu(H_2O)_2(en)_2]^{2+}[(HL^3)^-]_2$  (3), appears.

Yield, 76% (based on Cu). Anal. Calcd. for  $C_{24}H_{36}CuN_{10}O_{10}S_2$  (M = 752.2): C, 38.32; H, 4.82; N, 18.62. Found: C, 38.26; H, 4.80; N, 18.65. IR, cm<sup>-1</sup>: 3446, 3344, 3297 and 3263 v(OH), 3105 and 2963 v (NH), 2212 v(C=N) 1665 v(C=O), 1591 v(C=N).



Fig. 3.10: New copper complex 3.

## 3.3.3.2 Silver Complex synthesis 4

Silver nitrate (AgNO<sub>3</sub>) (0.34 g, 2 mmol) and 0.2 mL of nitric acid (HNO<sub>3</sub>) were added to a solution of NaHL<sup>3</sup> (0.29 g, 1 mmol) in MeOH (30 mL). The reaction mixture was evaporated slowly at room temperature to favoured the formation of crystals. After two days, orange crystals of  $[Ag_2(\mu - HL^3)_2]_n \cdot nH_2O$  (4), appears.

Yield, 70% (based on Ag). Anal. Calcd. for  $C_{20}H_{18}Ag_2N_6O_9S_2$  (M = 766.3): C, 31.35; H, 2.37; N, 10.97. Found: C, 31.52; H, 2.02; N, 10.81. Found: IR, cm<sup>-1</sup>: 3453 v(OH), 3101 and 2999 v (NH), 2236 v(C=N), 1656 v(C=O) and 1588 v(C=N).



Fig. 3.11: New silver complex 4.

### 3.3.3.3 Copper Complex synthesis 5

Copper acetate  $Cu(CH_3COO)_2 H_2O$  (0.20 g, 1 mmol) and 0.2 mLqq2q of ethylendiamine was added to a solution of NaHL<sup>3</sup> (0.26 g, 1 mmol) in MeOH (30 mL). The reaction mixture was evaporated slowly at room temperature to favoured the formation of crystals. After one day, greenish–black crystals of  $[Cu(en)_2(\mu-L^3)^2]_{2n} H_2O$  (5) appears.

Yield, 74% (based on Cu). Anal. Calcd. for  $C_{29}H_{52}Cu_2N_{14}O_9S_2$  (M = 932): C, 37.37; H, 5.62; N, 21.04. Found: C, 37.33; H, 5.16; N, 20.94. IR, cm<sup>-1</sup>: 3448 and 3316 v(OH), 2960 and 2890 v (NH), 2175 v(C=N), 1636 v(C=O), 1560 v(C=N).



Fig. 3.12: New copper complex 5.

# 3.4 Microwave-assisted solvent-free peroxidative oxidation of alcohols

Oxidation reactions of the alcohols were carried out in sealed cylindric Pyrex tubes under focused microwave irradiation as follows: the alcohol (2.5 mmol), 1-10  $\mu$ mol of the metallic catalyst precursor and a 70% aqueous solution of *t*-BuOOH (5 mmol) were introduced in the tube. This was then placed in the microwave reactor and the system was left under stirring and under irradiation (5-10 W), at 80 - 150 °C, for 0.5 -2 h. After cooling to room temperature, 150  $\mu$ L of benzaldehyde (internal standard) and 2.5 mL of NCMe (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min and then a sample (1  $\mu$ L) was taken from the organic phase and analysed by GC using the internal standard method. After did the calibration curve, 1  $\mu$ L of reaction mixture was inject in the GC machine, the separation take place in 10 minutes. The program used for this analysis involve the change of temperature during the separation, we start from 140°C to 240°C, in this way, we can separate all component of the reaction mixture.

In figure 3.13 is reported an example of final chromatogram, is possible to see that the first pick correspond to the solvent, after 5 minutes more or less, the pick of internal standard appear, and after 6-7 minutes the final product (acetophenone) appear, of course, some alcohol remain unreacted. At this point, in base on the area of the pick and from the retention time, is possible to know the amount of final product and so, calculate the yield of the reaction.



Fig.3.13: Example of chromatogram

Was also tested for activity of five different additives; TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (62.5  $\mu$ mol); 1M K<sub>2</sub>CO<sub>3</sub> (62.5  $\mu$ mol); nitric acid 1M HNO<sub>3</sub> (62.5  $\mu$ mol); radical trap CBrCl<sub>3</sub> (2.5 mmol); radical trap Ph<sub>2</sub>NH (2.5 mmol).

Was also tested for activity of different oxidant like hydrogen peroxide  $H_2O_2$  30% ( 5 mmol) and different substrate; 2-hexanol (2.5 mmol); 3-hexanol (2.5 mmol); cyclohexane (2.5 mmol) and benzyl alcohol (2.5 mmol).

# 4. RESULT AND DISCUSSION 4.1 Characterization of ligand NaHL<sup>1</sup> and complex 1

The new SAHAMCs ligands NaHL<sup>1</sup>, were synthesized via the Japp–Klingemann reaction between the respective aromatic diazonium salt and malononitrile in an ethanol solution containing sodium acetate (Scheme 4.1). The Japp-Klingemann reaction, is a good method to produce SAHAMCs with a very good yield for this reaction.



Scheme 4.1: Synthesis of NaHL<sup>1</sup>

The first step is the formation of the diazonium salt by reacting the ammine, in this particular case 2aminobenzenesulfonic acid, with sodium nitrate and hydrocloridric acid carried out in water medium in a cooled bath in order to maintain the temperature under 5°C to avoid the reactivity of diazonium salt that is formed. This step in general take more or less 3 hours.

When the first step going to the end, is possible to prepare the second reagent by simple dissolution of malononitrile in ethanol containing sodium acetate.

After mixing of the two solution is possible to see a yellow precipitate in the solution.

After filtration, the compound was characterized by different technique.

The ligand result soluble in DMSO, MeOH, Acetone and water.

The <sup>1</sup>H-NMR spectrum of NaHL<sup>1</sup> in dimethylsulfoxide- $d^6$  solution at room temperature shows a signal at  $\delta$  13.33 assigned to the proton of the protonated nitrogen atom adjacent to the aryl unit (=N-NH- hydrazone form). Moreover, the <sup>13</sup>C-NMR in dimethylsulfoxide- $d^6$  solution at room temperature shows a signal at  $\delta$  113.6 assigned to the carbon attach to the nitrogen in C=N moiety. The IR spectrum of the isolated NaHL<sup>1</sup> shows the NH vibrations at 3099 cm<sup>-1</sup>. The vibration of two nitrile group, v(C=N) at 2218 cm<sup>-1</sup> and 2227 cm<sup>-1</sup> and v(C=N) at 1587 cm<sup>-1</sup>.

The H in NH attach to the aryl group can form hydrogen bond with the O of sulfonic group to form a six membered ring with the formation of the hydrazo form (Scheme 4.2).

One-pot template condensation of sodium 2-(2-(dicyanomethylene)hydrazinyl) benzenesulfonate (NaHL<sup>1</sup>) with water on manganese(II) acetate tetrahydrate, led to a mononuclear complex,

 $[Mn(H_2O)_6][HL^{1a}]_2 \cdot 4H_2O$  (1), where  $HL^{1a} = 2 \cdot (SO_3^{-}) - C_6H_4 - (NH)N = C(C \equiv N)[C(=O)(NH_2)]$  is the ligand derived from nucleophilic attack of water (a) on a cyano group of NaHL<sup>1</sup>, giving the corresponding carboxamide (HL<sup>1a</sup>) (Scheme 4.2).



Scheme 4.2: Sinthesis of complex 1

Elemental analysis and X-ray method (see below) are support the formulation, while the IR revels v(C=N) at 2214 cm<sup>-1</sup>, v(C=O) and v(C=N) at 1697 cm<sup>-1</sup> and 1589 cm<sup>-1</sup>. From comparison of the IR of the ligand and the IR of the complex is possible to see the difference in the representative peak that confirm that the crystals are different from the ligand (Figure 4.1).





**Fig. 4.1:** IR of NaHL<sup>1</sup>, IR of complex **1**.

The crystal structure of **1** (Figure 4.2) consist of organic anionic moieties with, independent Mn cationic center with distorted octahedral geometry filled with water ligands. An interesting feature of **1** consists in the extensive hydrogen bonding that arises from the coordinated water molecules; each of the equatorial ones repeatedly acts as a double H-bond donor to one vicinal organic group, while each of the apical ones contacts with a non-coordinated water molecule and another organic moiety. This results in the extensive interlinkage of every hexaaqua-Mn(II) unit with six L<sup>1a</sup> groups and two water molecules, thus leading to a 3D supramolecular framework solely based on non-covalent contacts.



Fig. 4.2: X-ray structure of 1.

## 4.2. Characterization of ligand Na<sub>2</sub>H<sub>2</sub>L<sup>2</sup> and complex 2

The new SAHAMCs ligands  $Na_2H_2L^2$ , were synthesized via the Japp–Klingemann reaction between the respective aromatic diazonium salt and pentane-2,4-dione in an ethanol solution containing sodium acetate (Scheme 4.3).



Scheme 4.3: Synthesis of Na<sub>2</sub>H<sub>2</sub>L<sup>2</sup>.

The first step is the formation of the diazonium salt by reacting the aromatic amine, in this particular case 2-aminobenzenesulfonic acid, with sodium nitrate and hydrocloridric acid carried out in water medium in a cooled bath in order to maintain the temperature under 5°C to avoid the reactivity of diazonium salt that is formed. This step in general take more or less 3 hours.

When the first step going to the end, is possible to prepare the second reagent by simple dissolution of 5,5-dimethylcyclohexane-1,3-dione in ethanol containing sodium acetate. After mixing of the two solution is possible to see a red precipitate in the solution. After filtration, the compound was characterized by different technique. The ligand result soluble in DMSO, MeOH, Acetone and water.

The <sup>1</sup>H-NMR spectrum of Na<sub>2</sub>H<sub>2</sub>L<sup>2</sup> in dimethylsulfoxide- $d^6$  solution at room temperature shows a signal at  $\delta$  14.17 assigned to the proton of the protonated nitrogen atom adjacent to the aryl unit (=N-NH- hydrazone form). Moreover, the two methyl groups of the 5,5-dimethylcyclohexane-1,3-dione moiety yield separate singlets in the proton spectrum. Those data support the formation of the hydrazo form (Scheme 4.2) with a six-membered H-bonded ring involving one of the carbonyl groups and the protonated nitrogen moiety of the hydrazone structure. The IR spectrum of the isolated Na<sub>2</sub>H<sub>2</sub>L<sup>2</sup> shows the OH and NH vibrations at 3459 and 2957 cm<sup>-1</sup>, respectively. v(C=O) (1648 cm<sup>-1</sup>), v(C=O···H) (1592 cm<sup>-1</sup>) and v(C=N) (1494 cm<sup>-1</sup>) also support the H-bonded hydrazone structure in the solid state.

Complex  $[Cu(H_2O)Cu(H_2O)_4(\mu L^2)]_2 \cdot 2H_2O$  (2) derived from reactions with Na<sub>2</sub>H<sub>2</sub>L<sup>2</sup> with copper(II) nitrate hydrate, were isolated and characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. A slow evaporation of a mixture of copper(II) nitrate hydrate in a solution of in MeOH/water give greenish–black crystals of the (2) (Scheme 4.4).



Scheme 4.4: Synthesis of complex 2.

Elemental analysis is support the formulation, while the IR reveals v(C=O) 1637 cm<sup>-1</sup>, v(C=O) 1589 cm<sup>-1</sup>, and v(C=N) 1498 cm<sup>-1</sup>. From comparison of the IR of the Na<sub>2</sub>H<sub>2</sub>L<sup>2</sup> with the **2** is possible to see the difference in the representative peak that confirm that the crystals are different from the ligand (Figure 4.3).





Fig. 4.3: IR of  $Na_2H_2L^2$  and 2, respectively.

 $[Cu(H_2O)Cu(H_2O)_4(\mu-L^2)]_2$  ·2H<sub>2</sub>O (2) crystallizes as tetranuclear species, with one and four water molecules and two main ligands, the coordination environment of two Cu(II) is square-pyramidal and other two is distorted octahedral geometry (Figure 4.4). being bonded to a hexadentate  $\mu$ -L<sup>2</sup> ligand with donor atoms, the N-hydrazone atoms N(1) and N(2), the oxygen atoms (O2 and O3), (O1) and (O11) from the carbonyl, alchoxy and sulfo. The coordination spheres are completed via the oxygen atoms (O4, O5, O6, O7 and O8) of water molecules.



Fig. 4.4: X-ray structure of 2.

# 4.3. Characterization of ligand NaHL<sup>3</sup> and complexes 3, 4, 5

The new SAHAMCs ligands NaHL<sup>3</sup>, were synthesized via the Japp–Klingemann reaction between the respective aromatic diazonium salt and 3-aminocrotononitrile in an ethanol solution containing sodium hydroxide (Scheme 4.5).



Scheme 4.5: Synthesis of NaHL<sup>3</sup>, 3, 4 and 5.

The first step is the formation of the diazonium salt by reacting the amine, in this particular case 2aminobenzenesulfonic acid, with sodium nitrate and hydrochloric acid carried out in water medium in a cooled bath in order to maintain the temperature under 5°C to avoid the reactivity of diazonium salt that is formed. This step in general take more or less 3 hours.

When the first step going to the end, is possible to prepare the second reagent by simple dissolution of 3-aminocrotononitrile in ethanol containing sodium hydroxide. After mixing of the two solution is possible to see a orange precipitate in the solution. After filtration, the compound was characterized by different technique. The ligand result soluble in DMSO, MeOH, Acetone and water. NaHL<sup>3</sup> exists in DMSO solution as a mixture of two isomeric *E*- and *Z*-hydrazone forms, the former involving a two-centered RAHB system and the later a three-centered one (Scheme 4); the <sup>1</sup>H NMR shifts of the N–H···O proton, characteristic for the two- and three-centred RAHB systems, are clearly observed as singlets at 12.72 and 14.04 ppm, respectively. Thus, the stabilization of the N–H proton by RAHB

hampers its exchange with H<sub>2</sub>O present as moisture in DMSO. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of NaHL<sup>1</sup> contains two sets of peaks, with two C=N resonances at 110.69 and 116.15 ppm for *E*-hydrazone and *Z*-hydrazone, respectively. This fact confirms the rotation of the active methylene derived fragment around the C=N double bond (*E*/*Z* isomerization).

The new copper(II),  $[Cu(H_2O)_2(en)_2]^{2+}[(HL^3)]_2$  (**3**),  $[Cu(en)_2(\mu-L^3)^2]_{2n} \cdot nH_2O$  (**5**) and silver(I),  $[Ag_2(\mu-HL^3)_2]_n \cdot nH_2O$  (**4**) complexes are isolated by reaction of NaHL<sup>3</sup> with Cu(NO<sub>3</sub>)\_2·2.5H<sub>2</sub>O and AgNO<sub>3</sub> in presence of en and HNO<sub>3</sub>, respectively. All these complexes were characterized by elemental analysis, IR spectroscopy and X-ray analysis. Elemental analysis is support the formulation, while the IR reveals 3446, 3344, 3297 and 3263 v(OH), 3105 and 2963 v (NH), 2212 v(C=N) 1665 v(C=O), 1591 v(C=N) for **3**, 3453 v(OH), 3101 and 2999 v (NH), 2236 v(C=N), 1656 v(C=O) and 1588 v(C=N) for **4** and 3448 and 3316 v(OH), 2960 and 2890 v (NH), 2175 v(C=N), 1636 v(C=O), 1560 v(C=N) for **5**. From comparison of the IR of the NaHL<sup>3</sup> and of the **3-5** is possible to see the difference in the representative peak that confirm that the crystals are different from the ligand (Figure 4.5).







Fig. 4.5: IR of NaHL<sup>3</sup> 3, 4 and 5.

The asymmetric unit of  $[Cu(H_2O)_2(en)_2]^{2+}[(HL^3)]_2$  (3) comprises one anionic  $(HL^3)^-$  moiety, half of the  $[Cu(H_2O)_2(en)_2]^{2+}$  complex cation (the copper atom is on an inversion center) (Figure 4.6). The geometry of the  $(HL^3)^-$  anion is very close to that the related AHMACs ligands<sup>(64)</sup>, most of the atoms lying in the plane defined by the phenyl ring. The basal plane of the cationic moiety is formed by two bidentate en ligands while two water molecules occupy the axial positions. The Cu1–O1 bond distance of 2.561 Å is considerably longer than the equatorial Cu1–N1 and Cu1–N2 ones [2.000 and 2.020 Å, respectively]. This distortion is common for a d<sup>9</sup> Cu(II) ion and attributable to Jahn-Teller effects. Owing to the chelating effect of en, the metal presents a distorted octahedral geometry with endo and exo NCuN angles of 84.00 and 96.00°, respectively. The cationic and anionic units of **3** are gathered by intermolecular hydrogen interactions, the former owning the donor (N and O) atoms and the latter the acceptor ones, each cation consequently cooperating with six organic anions and each of these with two cations. Trapped in the so formed 3D metal organic network there are water molecules extensively involved in O–H…O interactions between each other and organized in infinite 1D chains along the crystallographic *b* axis.

The polymeric compound  $[Ag_2(\mu-HL^3)_2]_n \cdot nH_2O$  (4) bears dimeric  $[Ag_2(\mu-HL^3)_2]$  units, the positive charge of which is balanced by monodeprotonated  $(\mu-HL^3)^-$  ligands acting in different coordination modes (Figure 4.6). In 4 the structure of  $(\mu-HL^3)^-$  preserves the strong RAHB linking the NH-moiety of the hydrazone unit to an *O*-sulfonate group. Metal cations are in N of cyano and O atoms of sulfonate environments.

A new coordination polymer,  $[Cu(en)_2(\mu-L^3)^2]_{2n} \cdot nH_2O$  (5) are constructed by repetition of dinuclear unites  $[Cu(en)_2(\mu-L^3)^2]_2$  (Figure 4.6) via an oxygen atom of sulfonate group. The positive charges of  $Cu^{2+}$  are neutralized by deprotonated sulfo group and hydrazone unit. In 5, both copper atoms have distorted octahedral geometry, the fifth and sixth coordination positions of  $[Cu(en)_2]^{2+}$  are occupied by nitrogen and oxygen of nitrile sulfo groups, respectively.



Fig. 4.6: X-ray structure of 3, 4 and 5.

# 4.4 Catalytic activity of complex 1, 2, 3 in oxidation of alcohol

# 4.4.1 Catalytic activity and recycling experiment of complex 1-2 in an heterogeneous system.

Complexes **1** and **2** were tested as catalyst precursors for the oxidation of 1-phenylethanol (model substrate), using aqueous *tert*-butylhydroperoxide (Bu<sup>t</sup>OOH, TBHP, aq. 70%, 2 eq.) as oxidizing agent, under typical conditions of 150 °C, low power (10 W) microwave (MW) irradiation, 1 h reaction time and in a solvent- and additive-free medium (Scheme 2). These complexes exhibit good catalytic activity for the peroxidative oxidation 1-phenylethanol under the above conditions, leading to yields of acetophenone up to 76.0 % (**1**) or 85.5 % (**2**) (Table 1, entries 13 and 10, respectively), and turnover frequencies (TOF, moles of product per mol of catalyst per hour) up to 1.83 x 10<sup>-3</sup> (**1**) or 1.90 x 10<sup>3</sup> h<sup>-1</sup> (4.75 x 10<sup>2</sup> h<sup>-1</sup> per Cu atom, **2**) for a low catalyst loading (catalyst / substrate molar ratio of 0.04%) after 1 h under MW irradiation (Table 1, entries 11 and 13, respectively).

Moreover, these heterogeneous catalytic systems allowed their easy recovery and reuse, at least for three consecutive cycles, maintaining 89% of the initial activity and concomitant rather high selectivity (see below).



Scheme 4.6: MW-assisted oxidation of 1-phenylethanol to acetophenone catalysed by 1 or 2.

Complexes **1** and **2** were also tested towards the oxidation of other C<sub>6</sub> primary (benzyl alcohol) and secondary alcohols, namely cyclohexanol and the linear 2- and 3-hexanol. The ketones are the only oxidation products obtained (Table 2). As expected, the alicyclic cyclohexanol is less reactive than 1-phenylethanol: in the presence of a catalytic amount of **1** or **2** (0.4 mol% *vs.* substrate) and in the solvent- and additive-free medium, the systems yield 56.4% and 65.5% of cyclohexanone after 1 h at 150°C/10W MW irradiation (Table 2, entries 1 and 2, for **1** and **2**, respectively). The linear aliphatic alcohols 2-hexanol and 3-hexanol lead to similar (**1**) or lower (**2**) yields (Table 2, entries 3-6), under similar reaction conditions, as reported in other cases <sup>(65, 59, 66)</sup>.

While the copper 2/MW/TBHP oxidation system of the present study yields ketone products in the range of previously reported ones <sup>(65,59)</sup>, the Mn 1/MW/TBHP system is much more efficient then reported<sup>(66)</sup> homogeneous dinuclear Mn(II) complexes with Schiff bases /MW/TBHP oxidation of secondary alcohols, since it effectively operates in additive-free conditions and requires much lower loads of catalyst precursor.

The activity of **1** or **2** in the oxidation of benzyl alcohol is rather modest since only moderated 19% (**1**) or 24% (**2**) yields of benzaldehyde were obtained under the same reaction conditions (Table 2, entries 7 and 8, for **1** and **2**, respectively). The silica-supported manganese dioxide previously applied for the oxidation of benzyl alcohol under MW solvent-free conditions<sup>(67)</sup>, yielded 88% of benzaldehyde after 20 s irradiation. However, this system required an 5:1 molar excess of  $MnO_2$  relatively to the substrate.

| Entry           | Catalyst (amount,                       | Reaction | Temperature | Additive                             | Yield <sup>b</sup> | TON                      |
|-----------------|---|----------|-------------|--------------------------------------|--------------------|--------------------------|
|                 | mol% vs.                                | Time (h) | (°C)        | (mol% <i>v</i> s.                    | (%)                | [TOF (h⁻¹)] <sup>c</sup> |
|                 | substrate)                              |          |             | substrate)                           |                    |                          |
| 1               | <b>1</b> (0.4)                          | 0.5      | 80          | _                                    | 6.0                | 15 (30)                  |
| 2               | <b>1</b> (0.4)                          | 1        | 80          | _                                    | 11.1               | 28 (28)                  |
| 3               | 1 (0.4)                                 | 2        | 80          | _                                    | 14.7               | 37 (18)                  |
| 4               | <b>2</b> (0.4)                          | 0.5      | 80          | _                                    | 14.4               | 36 (72)                  |
| 5               | <b>2</b> (0.4)                          | 1        | 80          | _                                    | 21.1               | 52 (52)                  |
| 6               | <b>2</b> (0.4)                          | 2        | 80          | _                                    | 39.2               | 98 (49)                  |
| 7               | 1 (0.4)                                 | 1        | 120         | _                                    | 33.1               | 83 (83)                  |
| 8               | 1 (0.4)                                 | 1        | 150         | _                                    | 75.2               | 188 (188)                |
| 9               | <b>2</b> (0.4)                          | 1        | 120         | _                                    | 83.2               | 208 (208)                |
| 10              | <b>2</b> (0.4)                          | 1        | 150         | _                                    | 85.5               | 214 (214)                |
| 11              | 1 (0.04)                                | 1        | 150         | _                                    | 73.0               | 1.83×10 <sup>3</sup>     |
|                 | . ,                                     |          |             |                                      |                    | (1.83×10 <sup>3</sup> )  |
| 12              | <b>1</b> (0.2)                          | 1        | 150         | _                                    | 76.1               | 381 (381)                |
| 13              | <b>2</b> (0.04)                         | 1        | 150         | _                                    | 76.0               | 1.90×10 <sup>3</sup>     |
|                 |   |          |             |                                      |                    | (1.90×10 <sup>3</sup> )  |
| 14              | <b>2</b> (0.2)                          | 1        | 150         | _                                    | 78.2               | 391 (391)                |
| 15              | <b>1</b> (0.4)                          | 1        | 150         | K <sub>2</sub> CO <sub>3</sub> (2.5) | 38.1               | 95 (95)                  |
| 16              | <b>1</b> (0.4)                          | 1        | 150         | HNO <sub>3</sub> (2.5)               | 34.0               | 85 (85)                  |
| 17              | 1 (0.4)                                 | 1        | 150         | <b>TEMPO</b> (2.5)                   | 56.6               | 142(142)                 |
| 18              | 1 (0.4)                                 | 1        | 150         | Ph <sub>2</sub> NH (100)             | 9.7                | 24 (24)                  |
| 19              | 1 (0.4)                                 | 1        | 150         | CBrCl <sub>3</sub> (100)             | 33.1               | 83 (83)                  |
| 20              | <b>2</b> (0.4)                          | 1        | 150         | K <sub>2</sub> CO <sub>3</sub> (2.5) | 19.8               | 50 (50)                  |
| 21              | <b>2</b> (0.4)                          | 1        | 150         | HNO <sub>3</sub> (2.5)               | 43.7               | 109 (109)                |
| 22              | <b>2</b> (0.4)                          | 1        | 150         | <b>TEMPO</b> (2.5)                   | 58.1               | 145 (145)                |
| 23              | <b>2</b> (0.4)                          | 1        | 150         | Ph <sub>2</sub> NH (100)             | 5.6                | 14 (14)                  |
| 24              | <b>2</b> (0.4)                          | 1        | 150         | CBrCl <sub>3</sub> (100)             | 33.7               | 84 (84)                  |
| 25 <sup>d</sup> | <b>1</b> (0.4)                          | 1        | 150         | _                                    | 3.0                | 8 (8)                    |
| 26 <sup>e</sup> | Cu(NO <sub>3</sub> ) <sub>2</sub> (0.4) | 1        | 150         | _                                    | 18.2               | 46 (46)                  |
| 27 <sup>e</sup> | Mn(CH <sub>3</sub> COO) <sub>2</sub>    | 1        | 150         | _                                    | 16.9               | 42 (42)                  |
|                 | (0 4)                                   |          |             |                                      |                    | · · /                    |

**Table 1:** Selected results for the solvent-free MW-assisted oxidation of 1-phenylethanol using **1** or **2** as catalyst precursors.<sup>*a*</sup>

<sup>a</sup> Reaction conditions unless stated otherwise: 2.5 mmol of 1-phenylethanol, 1-10  $\square$ mol (0.04 – 0.4 mol% vs. substrate) of 1 or 2, 5 mmol of TBHP (2 eq., 70% in H<sub>2</sub>O), 80 – 150 °C, MW irradiation (5-10 W power). <sup>b</sup> Molar yield (%) based on substrate, *i.e.* moles of acetophenone per 100 mol of 1-phenylethanol determined by GC. <sup>c</sup> Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets). <sup>d</sup> 5 mmol of H<sub>2</sub>O<sub>2</sub> (30% aqueous solution) instead of TBHP. <sup>e</sup> Included for comparative purposes.

| Entry | Catalyst | Substrate     | Product       | Yield<br>(%) <sup>b</sup> | TON<br>[TOF(h <sup>-1</sup> ] <sup>c</sup> |
|-------|----------|---------------|---------------|---------------------------|--|
| 1     | 1        | Qualabayanal  | Cyclohexanone | 56.4                      | 141 (141)                                  |
| 2     | 2        | Cyclonexanol  |               | 65.5                      | 164 (164)                                  |
| 3     | 1        | 2 Hoverol     | 2-Hexanone    | 60.3                      | 151 (151)                                  |
| 4     | 2        | 2-nexanoi     |               | 52.4                      | 131 (131)                                  |
| 5     | 1        | 2 Hovenel     | 3-Hexanone    | 55.5                      | 139 (139)                                  |
| 6     | 2        | 3-Hexanol     |               | 37.1                      | 93 (93)                                    |
| 7     | 1        | Ronzylalcohol | Bonzaldabuda  | 24.0                      | 60 (60)                                    |
| 8     | 2        | Benzyialconol | Benzaidenyde  | 19.1                      | 48 (48)                                    |

**Table 2:** Selected results for the solvent-free MW-assisted oxidation of selected  $C_6$  secondary alcohols and of benzylalcohol using **1** and **2** as catalyst precursors<sup>a</sup>

<sup>a</sup> Reaction conditions (unless stated otherwise: 2.5 mmol of substrate, 5 mmol of Bu<sup>t</sup>OOH (aq. 70%), 10  $\square$ mol (0.4 mol% *vs.* substrate) of **1** or **2**, 150 °C, 1h of microwave irradiation (10 W). <sup>b</sup> Molar yield (%) based on substrate, *i.e.* moles of product per 100 mol of substrate determined by GC. <sup>c</sup> Turnover number = number of moles of product per mol of metal catalyst; TOF = TON per hour

<sup>c</sup> Turnover number = number of moles of product per mol of metal catalyst; TOF = TON per hour (values in brackets).

The influence of various reaction parameters such as the amount of catalyst precursor and oxidant, type of oxidant, time, temperature and presence of additives were investigated for the most active substrate (1-phenylethanol), and the results are summarized in Table 1 and Figures 4.7 - 4.9.

The microwave-assisted alcohol oxidation depends strongly on the temperature (Figure 4.7). For example, a high yield of 85.5% of acetophenone is achieved after 1 h at 150 °C (5 W) for the copper system **2** without any additive (Table 1, entry 10), which is much higher than the 21.1 % yield obtained for the same reaction time but at 80 °C (Table 1, entry 5). Furthermore, at this temperature, only 39.2% (**2**) or 14.7% (**1**) of acetophenone is obtained for the extended reaction time of 2 h (Table 1, entries 6 and 3, respectively).



Fig. 4.7: Influence of the temperature on the yield of acetophenone from MW-assisted proxidative oxidation of 1-phenylethanol catalysed by 1 or 2.

The influence of the amount of **1** and **2** on the yield and TON (or TOF) was studied (entries 8 and 10-14, Table 1, Figure 3). While an amount increase of **1** does not appear to have a significant effect on the acetophenone yield, the increase of **2** results in a yield enhancement, *e.g.* from 76.0% to 85.5% upon changing the amount of catalyst from 1  $\square$ mol (0.04% *vs.* substrate) to 10  $\square$ mol (0.4 mol% *vs.* substrate). As expected, the increase of the catalysts amounts results in a corresponding TON lowering for both **1** and **2** (Figure 4.8).



Fig. 4.8: Effect of the amount of catalysts 1 and 2 on the yield (solid lines) and turnover number (TON) (dotted lines) for the oxidation of 1-phenylethanol to acetophenone.

For **1**, experiments with the cheaper and environmentally friendly hydrogen peroxide (30% aqueous solution) as oxidant are not effective, as attested by the marked yield lowering *e.g.* from 85.5% to 3.0% (entry 25, Table 1), in accord with the expected decomposition of  $H_2O_2$  under the used reaction conditions (150 °C). In the case of **2**, the reaction was extremely exothermic and so, was not possible to performed that reaction in MW, Probably, in presence of compound **2**,  $H_2O_2$  going to react very strongly with the catalyst precursor and this aspect has made impossible to test the hydrogen peroxide with this compounds.

The influence of the presence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), a nitroxyl radical that is a known <sup>(65,59,67,68)</sup> promoter in oxidation catalysis of alcohols, was also investigated. Surprisingly, a significant yield decrease (Figure 4.9) was observed for the 1-phenylethanol oxidation from 75.2% and 85.5% in the absence of TEMPO (for 1 and 2, respectively, entries 8 and 10, Table 1) to 56.6% (1) or 58.1% (2) in its presence (entries 17 and 22, Table 1).

Moreover, the previously recognised promoting effect of basic additives  $^{(65,69,70,71,72)}$  is not observed for the present catalytic systems; in contrast, addition of 1 M solution of K<sub>2</sub>CO<sub>3</sub> hampers the reaction (Table 1, entries 15 and 20; Figure 4.9). The presence of HNO<sub>3</sub> also exhibited an inhibitory effect on the acetophenone yield (Table 1, entries 16 and 21, Figure 4.9), as found *e.g.*, for the MW-assisted oxidation of 1-phenylethtanol with TBHP catalysed by the Cu(II) complex  $[Cu(H_2R)(HL)]$ ·H2O [H2L = (E)-2-(((1-hydroxynaphthalen-2-yl)methylene)amino)benzenesulfonic acid]<sup>(59)</sup> or Cu(II) complexes bearing the 1,6-bis(2'-pyriyl)-2,5-dithiahexane ligand<sup>(71,73)</sup>. In fact, the mechanism of alcohol oxidation with TBHP does not seem to require the presence of protons as verified<sup>(74,75)</sup> in the oxidation of 1-phenylethanol with TBHP catalysed by bi- or tetra-nuclear cage-like copper(II) silsesquioxanes.





A very strong inhibition effect is observed (Figure 4.9) when the peroxidative oxidation of 1phenylethanol is carried out in the presence of either an oxygen-radical trap such as  $Ph_2NH$  (Table 1, entries 18 (1) or 23 (2)) or a carbon-radical trap such as  $CBrCl_3$  (Table 1, entries 19 (1) or 24 (2)). This suggests that the oxidation reaction proceeds mainly via a radical mechanism which involves both oxygen- and carbon-centred radicals. It may involve *e.g.*, *t*BuO<sup>•</sup> radicals produced in the Mn or Cu promoted decomposition of TBHP<sup>(65)</sup>. It may proceed via the coordination of the alcohol substrate to an active site of the catalyst, and its deprotonation to form the alkoxide ligand, followed by a metalcentred dehydrogenation<sup>(70,72,76)</sup>.

#### Catalyst recycling

Catalyst recyclability was investigated for up to three consecutive cycles for both catalyst precursors, **1** and **2**. On completion of each stage, the product was analyzed as usually and the catalyst was recovered by filtration from the reaction mixture, thoroughly washed and dried. The subsequent cycle was initiated upon addition of new standard portions of all other reagents. The filtrate was tested in a new reaction (by addition of fresh reagents), and no oxidation products were detected. Figure 4.10 shows the recyclability of the systems: in the second cycle **1** maintains almost (99.5%) the original

level of activity, and **2** achives 91.8% of its initial one. In the third consecutive reaction cycle 89% of the initial activity is still exhibited by both complexes, with a rather high selectivity to acetophenone.



Fig. 4.10: Effect of the catalyst recycling on the yield of acetophenone from MW-assisted peroxidative oxidation of 1-phenylethanol catalysed by 1 and 2.

After each cycle, a little amount of catalyst precursor residue was taken to make different analysis like IR, UV-visible, TGA and X-Ray Powder diffraction to check if the compounds are the same after reaction.

From the IR spectroscopy (figure 4.11) is possible to see that in both catalyst precursor **1** and **2**, the main different after three cycle was in the intensity of the bands, no significant shift was recorded for these compounds. Some little shift are possible to recognize but is not so relevant. These shifts are probably due to the coordination of some molecules of alcohol at the metal center but from this previous screen we can say that the catalyst precursor not undergo significant changes. More investigation was performed by UV-Visible comparing ligand NaHL<sup>1</sup> andNa2H2L<sup>2</sup>, catalyst precursor **1** and **2** before the reaction and after each cycles (Figure 4.12).





Fig. 4.11: IR for three cycles about compound 1 and 2.

From the first UV spectra, is possible to see that the catalyst precursor **1**, after the three catalytic cycles remain unchanged (last three lines at the bottom of the picture). But, comparing catalyst precursor before and after reaction is possible to see that the absorption was completely different. This suggest that during the reaction, catalyst precursor **1** start to decomposed in something. Probably, TBHP can react with catalyst precursor to generate some species that are different to identify, but we can say that this new species are active because the yield doesn't change to much. About catalyst precursor **2**, comparing the absorbance between the catalyst precursor **2** before the reaction and after one cycle, is possible to see that only a little shift in the value of maximum absorption was observed, but, after two and three cycles, also **2** start to decompose. Also in this case we can affirm that the new species are active.





Fig. 4.12: UV-Visible about recycling experiment of catalyst precursor 1 and 2.

Thermo gravimetric analysis was also performed for both catalyst precursor **1** and **2**, before and after catalysis. In figure 4.13 was reported the TGA about **1** and in figure 4.13 about **2**. Is possible to observe the variation of the mass of sample when the temperature increase. It's means that the compound start to decompose at higher temperature.





Fig. 4.13: Thermogram of 1 before and after catalytic cycle respectively.

In the case of **2**, some little explosion happens during the analysis. The same thing happens with the strong oxidant. This fact confirm that the oxidant react with the complex in particular when the temperature increase.




Fig. 4.14: Thermogram of 2 before and after catalytic cycle respectively.

X-Ray powder diffraction was also used to investigate the catalyst precursor after catalytic cycle. This analysis was possible only for **2** because the catalyst precursor residue of **1** wasn't a crystalline powder. From the diffractogram (figure 4.15), is possible to see that **2** after catalysis contain again the metal Cu.



Fig. 4.15: X-Ray powder diffraction of 2.

### 4.4.2 Catalytic activity of complex 3

Complexes **3** was tested as catalyst precursor for the oxidation of 1-phenylethanol (model substrate), using aqueous *tert*-butylhydroperoxide (Bu<sup>t</sup>OOH, TBHP, aq. 70%, 2 eq.) as oxidizing agent, under typical conditions of 150 °C, low power (10 W) microwave (MW) irradiation, 1 h reaction time and in a solvent- and additive-free medium (Scheme 2). These complex exhibit good catalytic activity for the peroxidative oxidation 1-phenylethanol under the above conditions, leading to yields of acetophenone up to 76.0 % (**3**) (Table 3, entry 8,), and turnover frequencies (TOF, moles of product per mol of catalyst per hour) up to  $1.8 \times 10^3$  (**3**) for a low catalyst loading (catalyst / substrate molar ratio of 0.04%) after 1 h under MW irradiation (Table 3, entry 11).

**Table 3:** Selected results for the solvent-free MW-assisted oxidation of 1-phenylethanol using **3** as catalyst precursor.<sup>*a*</sup>

| Entry           | Catalyst                                | Reaction | Temperature    | Additive                             | Yield <sup>b</sup> | TON                        |
|-----------------|---|----------|----------------|--------------------------------------|--------------------|----------------------------|
| Lindy           | (amount mol%                            | Time (b) | (0C)           | (mol% vs                             | (%)                |                            |
|                 | (amount, mor/o                          |          | $(\mathbf{C})$ | (IIIOI/0 VS.                         | (70)               |                            |
|                 | vs. substrate)                          |          |                | substrate)                           |                    |                            |
| 1               | <b>3</b> (0.4)                          | 0.5      | 80             | -                                    | 9.9                | 25 (50)                    |
| 2               | <b>3</b> (0.4)                          | 1        | 80             | _                                    | 22.5               | 56 (56)                    |
| 3               | <b>3</b> (0.4)                          | 2        | 80             | _                                    | 41.4               | 104 (52)                   |
| 3               | <b>3</b> (0.4)                          | 1        | 120            | _                                    | 79.5               | 199 (199)                  |
| 4               | <b>3</b> (0.4)                          | 1        | 150            | _                                    | 73.3               | 202 (202)                  |
| 5               | <b>3</b> (0.04)                         | 1        | 150            | _                                    | 72.0               | 1.8 x 10 <sup>3</sup> (1.8 |
|                 |   |          |                |                                      |                    | x10 <sup>3</sup> )         |
| 6               | <b>3</b> (0.2)                          | 1        | 150            | _                                    | 80.9               | 405 (405)                  |
| 7               | <b>3</b> (0.4)                          | 1        | 150            | K <sub>2</sub> CO <sub>3</sub> (2.5) | 31.0               | 78 (78)                    |
| 8               | <b>3</b> (0.4)                          | 1        | 150            | HNO <sub>3</sub> (2.5)               | 55.0               | 138 (138)                  |
| 9               | <b>3</b> (0.4)                          | 1        | 150            | TEMPO                                | 46.0               | 115 (115)                  |
|                 |   |          |                | (2.5)                                |                    |                            |
| 10              | <b>3</b> (0.4)                          | 1        | 150            | Ph₂NH                                | 5.0                | 13 (13)                    |
|                 |   |          |                | (100)                                |                    |                            |
| 11              | <b>3</b> (0.4)                          | 1        | 150            | CBrCl <sub>3</sub>                   | 24.0               | 60 (60)                    |
|                 |   |          |                | (100)                                |                    |                            |
| 26 <sup>e</sup> | Cu(NO <sub>3</sub> ) <sub>2</sub> (0.4) | 1        | 150            | _                                    | 18.2               | 46 (46)                    |

<sup>a</sup> Reaction conditions unless stated otherwise: 2.5 mmol of 1-phenylethanol, 1-10  $\Box$ mol (0.04 – 0.4 mol% *vs.* substrate) of **3**, 5 mmol of TBHP (2 eq., 70% in H<sub>2</sub>O), 80 – 150 °C, MW irradiation (5-10 W power). <sup>b</sup> Molar yield (%) based on substrate, *i.e.* moles of acetophenone per 100 mol of 1-phenylethanol determined by GC. <sup>c</sup> Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets).

The influence of various reaction parameters such as the amount of catalyst precursor and oxidant, type of oxidant, time, temperature and presence of additives were investigated for the 1-phenylethanol, and the results are summarized in Table 3 and Figures 4.15 - 4.17.

The microwave-assisted alcohol oxidation depends strongly on the temperature (Figure 4.16). For example, a high yield of 80.9% of acetophenone is achieved after 1 h at 150 °C (5 W) for the copper system **3** without any additive (Table 3, entry 8), which is much higher than the 22.5 % yield obtained for the same reaction time but at 80 °C (Table 3, entry 2).



### Temperature (°C)

Fig. 4.16: Influence of the temperature on the yield of acetophenone from MW-assisted peroxidative oxidation of 1-phenylethanol catalysed by 3.

The influence of the amount of **3** on the yield and TON (or TOF) was studied (entries 8 and 11-12, Table 3, Figure 4.17). T increase of **3** results in a yield enhancement, *e.g.* from 72.0% to 80.9% upon changing the amount of catalyst from 1  $\Box$ mol (0.04% *vs.* substrate) to 10  $\Box$ mol (0.4 mol% *vs.* substrate). As expected, the increase of the catalysts amounts results in a corresponding TON lowering for **3** (figure 4.16).



Fig. 4.17: Effect of the amount of catalyst 3 on the yield (solid lines) and turnover number (TON) (dotted lines) for the oxidation of 1-phenylethanol to acetophenone.

In the case of **3**, the change in the oxidant using  $H_2O_2$  instead of TBHP, result in a reaction extremely exothermic and so, was not possible to performed that reaction in MW, Probably, in presence of compound **3**,  $H_2O_2$  going to react very strongly with the catalyst precursor and this aspect has made impossible to test the hydrogen peroxide with this compounds.

The influence of the presence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), a nitroxyl radical that is a known <sup>(65,59,67,68)</sup> promoter in oxidation catalysis of alcohols, was also investigated. Surprisingly, a significant yield decrease (Figure 4.18) was observed for the 1-phenylethanol oxidation from 80.9% in the absence of TEMPO (for **3** entry 8, Table 3) to 46% (**3**) in its presence (entry 17, Table 3).

Moreover, the previously recognised promoting effect of basic additives  $^{(65,69,70,71,72)}$  is not observed for the present catalytic systems; in contrast, addition of 1 M solution of K<sub>2</sub>CO<sub>3</sub> hampers the reaction (Table 3, entry 15; Figure 4.18). The presence of HNO<sub>3</sub> also exhibited an inhibitory effect on the acetophenone yield (Table 3, entries 16, Figure 4.18), as found *e.g.*, for the MW-assisted oxidation of 1-phenylethtanol with TBHP catalysed by the Cu(II) complex [Cu(H<sub>2</sub>R)(HL)]·H2O [H2L = (*E*)-2-(((1hydroxynaphthalen-2-yl)methylene)amino)benzenesulfonic acid]<sup>(59)</sup> or Cu(II) complexes bearing the 1,6-bis(2'-pyriyl)-2,5-dithiahexane ligand<sup>(71,73)</sup>. In fact, the mechanism of alcohol oxidation with TBHP does not seem to require the presence of protons as verified<sup>(74,75)</sup> in the oxidation of 1-phenylethanol with TBHP catalysed by bi- or tetra-nuclear cage-like copper(II) silsesquioxanes.



#### Additive

**Fig. 4.18:** Influence of different additives (TEMPO, K<sub>2</sub>CO<sub>3</sub>, HNO<sub>3</sub>, radical traps) on the yield of acetophenone from MW-assisted peroxidative oxidation of 1-phenylethanol catalysed by **3**.

A very strong inhibition effect is observed (Figure 4.18) when the peroxidative oxidation of 1phenylethanol is carried out in the presence of either an oxygen-radical trap such as  $Ph_2NH$  (Table 3, entry 18) or a carbon-radical trap such as  $CBrCl_3$  (Table 3, entry 19). This suggests that the oxidation reaction proceeds mainly via a radical mechanism which involves both oxygen- and carbon-centred radicals. It may involve *e.g.*, *t*BuO<sup>•</sup> radicals produced in the Cu promoted decomposition of TBHP<sup>(65)</sup>. It may proceed via the coordination of the alcohol substrate to an active site of the catalyst, and its deprotonation to form the alkoxide ligand, followed by a metal-centred dehydrogenation<sup>(70,72,76)</sup>.

## **5. CONCLUSION**

The methods of synthesis of arylhydrazones of methylene active compounds (AHMACs) as well as the preparation and properties of their metal complexes are discussed in literature section. The rich organic chemistry of AHMACs makes them highly promising in the organic synthesis of compounds with interesting possible applications, namely related to their high propensity to tautomerism and isomerism. In many cases the coordination sphere of the metal ions can be completed with labile (e.g. solvent) molecules. Complexes with square planar, square pyramidal or octahedral geometries and with planar tridentate ONO-coordination sites are more common, but examples of other geometries and/or different NNO-, ONS-, OO- or NO-coordination motifs also exist.

The solubility in water of the AHMACs compounds has particular importance for catalysis and other applications where water is used as solvent and/or reactant. Incorporation of a hydrophilic polar (e.g., sulfo- or arseno-) group into the ligand is one of the common ways to increase the water solubility of its complexes; moreover, such a ligand is behave as a polydentate donor moiety, thus supporting an extension of coordination arrays in the solid state.

Thus in this Thesis we have synthesized two known sulfo functionalized AHMACs, 2-(2-(dicyanomethylene)hydrazinyl)benzenesulfonate (**NaHL**<sup>1</sup>) and 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-4-hydroxybenzene-1,3-disulfonate (**NaHL**<sup>2</sup>), and a new one (Z)-2-(2-(1-cyano-2-oxopropylidene)hydrazinyl)benzenesulfonate (**NaHL**<sup>3</sup>). Five new coordination compounds, [Mn(H<sub>2</sub>O)<sub>6</sub>][HL<sup>1a</sup>]<sub>2</sub>·4H<sub>2</sub>O (1), [Cu(H<sub>2</sub>O)Cu(H<sub>2</sub>O)<sub>4</sub>( $\mu$ -L<sup>2</sup>)]<sub>2</sub>·2H<sub>2</sub>O (2), [Cu(H<sub>2</sub>O)<sub>2</sub>(en)<sub>2</sub>]<sup>2+</sup>[(HL<sup>3</sup>)<sup>-</sup>]<sub>2</sub> (3), [Ag<sub>2</sub>( $\mu$ -HL<sup>3</sup>)<sub>2</sub>]<sub>n</sub>·nH<sub>2</sub>O (4) and [Cu(en)<sub>2</sub>( $\mu$ -L<sup>3</sup>)<sup>2-</sup>]<sub>2n</sub>·nH<sub>2</sub>O (5) are also isolated in solid state and fully characterized by using IR, elemental analysis and X-ray diffraction method. Template transformation of NaHL<sup>1</sup> with water on manganese(II) acetate tetrahydrate, leading to a new ligand HL<sup>1a</sup> = 2-(SO<sub>3</sub><sup>-</sup>)-C<sub>6</sub>H<sub>4</sub>-(NH)N=C(C=N)[C(=O)(NH<sub>2</sub>)], derived from nucleophilic attack of water (a) on a cyano group of NaHL<sup>1</sup>. It should be note that the first Ag<sup>1</sup>- AHMACs complex, [Ag<sub>2</sub>( $\mu$ -HL<sup>3</sup>)<sub>2</sub>]<sub>n</sub>·nH<sub>2</sub>O (4), is reported in this thesis.

Coordination environment of central atoms, nuclearity and supramolecular futures of the obtained complexes are depending on structure of ligands, metal ions, the amount of auxiliary ligand (on example of en) and reaction conditions.

Complexes 1 and 2 act as efficient and selective catalyst precursors for the mild MW-assisted oxidation of several  $C_6$  secondary alcohols in solvent- and additive-free systems, thus widening the scope of peroxidative catalytic systems suitable for MW assisted oxidative transformations of alcohols. A comparative study of their catalytic efficiency has been drawn towards the different alcohol substrates. Moreover, these heterogeneous catalytic systems allowed their easy recovery and reuse, at least for three consecutive cycles, maintaining 89% of the initial activity and concomitant rather high selectivity.

Complexes **3** also act as efficient and selective catalyst precursors for the mild MW-assisted oxidation of ssecondary alcohols in solvent- and additive-free systems, thus widening the scope of peroxidative catalytic systems suitable for MW assisted oxidative transformations of alcohols.

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