

# A Review Exploring the Coordination Chemistry of Active Methylene Groups Hydrazones

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## Review Article

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### ABSTRACT

Compounds possessing a methylene bridge located between two strong electron withdrawing groups (MACs, e.g., diketones, dinitriles, benzoyl acetonitriles, cyanothioacetamide, ethyl acetoacetate, diethyl malonate ethyl cyanoacetate, cyanoanilides, etc.) have also been of significant interest in coordination and organometallic chemistry of hydrazones, for instance, -diketones are important starting materials in many organic synthetic reactions, particularly in the perfume and cosmetic industries.

## INTRODUCTION

Aryl azocompounds (AACs) have ubiquitous motifs in heterocyclic chemistry and are widely utilized as azo dyes, PH-indicators, pigments, food additives, initiators for some radical reaction, therapeutic agents, etc. <sup>[1,2]</sup>. The coordination science of AACs has been extensively studied throughout the last decades on account of potential combination of important functional properties with a diversity of molecular structure of their complexes. Thereby, these complexes have attracted attention in various fields, such as synthesis of conducting and magnetic equipment's, Light-by-Light Scattering equipment's, supramolecular chemistry, biological activity, catalysis and bioinorganic chemistry of some complexes, among others <sup>[3-5]</sup>.

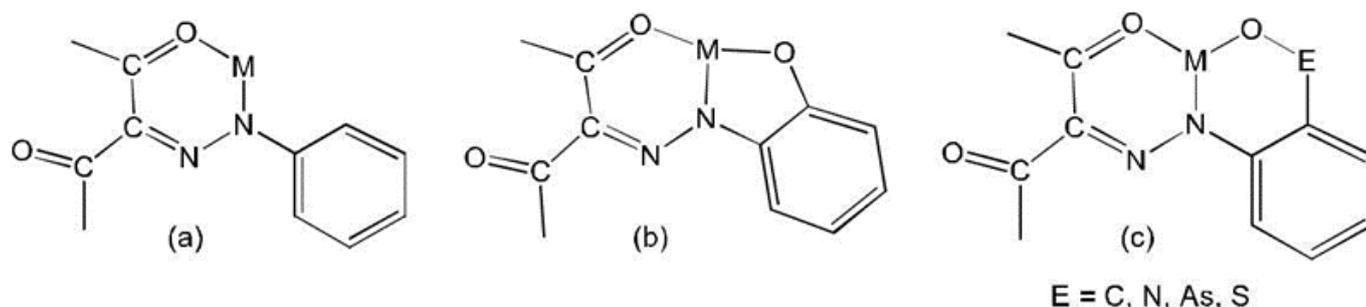
Compounds possessing a methylene bridge located between two strong electron withdrawing groups (MACs, e.g., diketones, dinitriles, benzoyl acetonitriles, cyanothioacetamide, ethyl acetoacetate, diethyl malonate ethyl cyanoacetate, cyanoanilides, etc.) have also been of significant interest in coordination and organometallic chemistry of hydrazones, for instance, -diketones are important starting materials in many organic synthetic reactions <sup>[3,4]</sup> particularly in the perfume and cosmetic industries <sup>[5]</sup>. Moreover, several representatives of MACs have been widely used in organic and organometallic chemistry for a long time and have recently been the object of increasing attention as components of multidentate ligands in metallo-supramolecular chemistry. Thus, the rich coordination chemistry of -diketones has been reviewed recently. The chemistry of cyano and ester-substituted MACs concerns such organic reactions as dimerization, hydrolysis, halogenation, reduction, carbonyl condensation hydrazones, ortho-ester and ylide formation; they are widely applied in industrial synthetics of, e.g., herbicides, corrosion inhibitors, dyes, polymers, washing and bleaching compositions, catalysis, lubricants, and optical sensitizers. Numerous inorganic template transformations <sup>[6-8]</sup> added an exciting interest on cyano-substituted MAC for metal-mediated preparation and coordination science.

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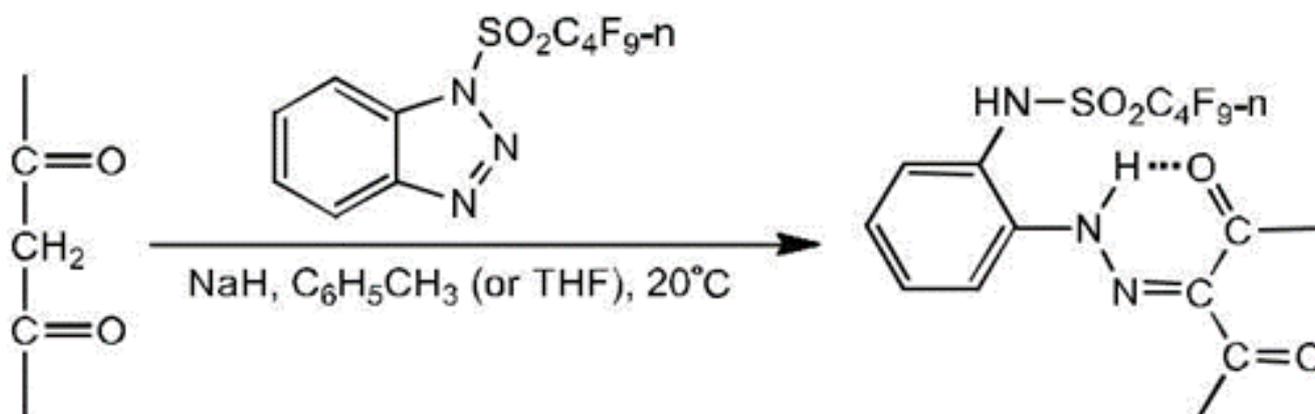
methylene bridge located between two strong electron withdrawing groups (MACs, e.g., diketones, dinitriles, benzoyl acetonitriles, cyanothioacetamide, ethyl acetoacetate, diethyl malonate ethyl cyanoacetate, cyanoanilides, etc.) have also been of significant interest in coordination and organometallic chemistry of hydrazones, for instance, -diketones are important starting materials in many organic synthetic, particularly in the perfume and cosmetic industries<sup>[11]</sup>. Moreover, several representatives of MACs have been widely used in organic and organometallic chemistry for a long time and have recently been the object of increasing attention as components of multidentate ligands in metallo-supramolecular chemistry. Thus, the rich coordination chemistry of -diketones has been reviewed recently. The chemistry of cyano and ester-substituted MACs concerns such organic reactions as dimerization, hydrolysis, halogenation, reduction, carbonyl condensation hydrazones, ortho-ester and ylide formation; they are widely applied in industrial synthetics of, e.g., herbicides, corrosion inhibitors, dyes, polymers, washing and bleaching compositions, catalysis, lubricants, and optical sensitizers. Numerous inorganic template transformations added an exciting interest on cyano-substituted MAC for metal-mediated preparation and coordination science.

### Literature Survey

The first methylene active arylhydrazones (**Scheme 1**) were reported as early as 1883, by Richter and Müntzer, then selected as "benzolazoacetone"<sup>[12]</sup> that was five years later represented by Japp and Klingemann to be an aryl-hydrazone. Until now, the synthesis of this category of AHMACs consists in the coupling of a MAC with an aromatic diazonium salt, mostly performed in methanolic, aqueous or ethanolic solution in presence of acetate as catalyst (**Scheme 2**)<sup>[13]</sup>. This reaction was considered very important that the title Japp-Klingemann became a standard reaction name<sup>[14]</sup>. In its course, the amine requires an early diazotization with an aqueous solution of sodium nitrite in acidic medium at very low temperature to produce the corresponding diazonium salt, which is very important part of the full Japp-Klingemann conversion. The earlier scheme underwent many modifications and improvements, e.g., higher yields of more pure products can be obtained when the coupling is undertaken in an alkaline medium such as solution of sodium hydroxide instead of sodium acetate (**Scheme 3**). On the other hand, the acidic medium used in the diazonium salt formation process strongly affects the yield and stability of diazonium salt.

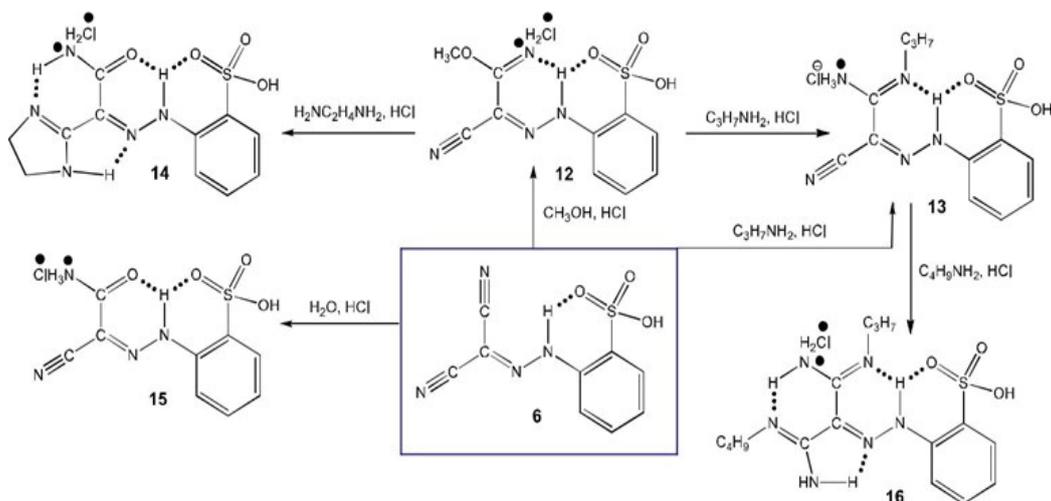


**Scheme 1.** Aromatic Hydrazones of methylene active compounds (AHMACs).

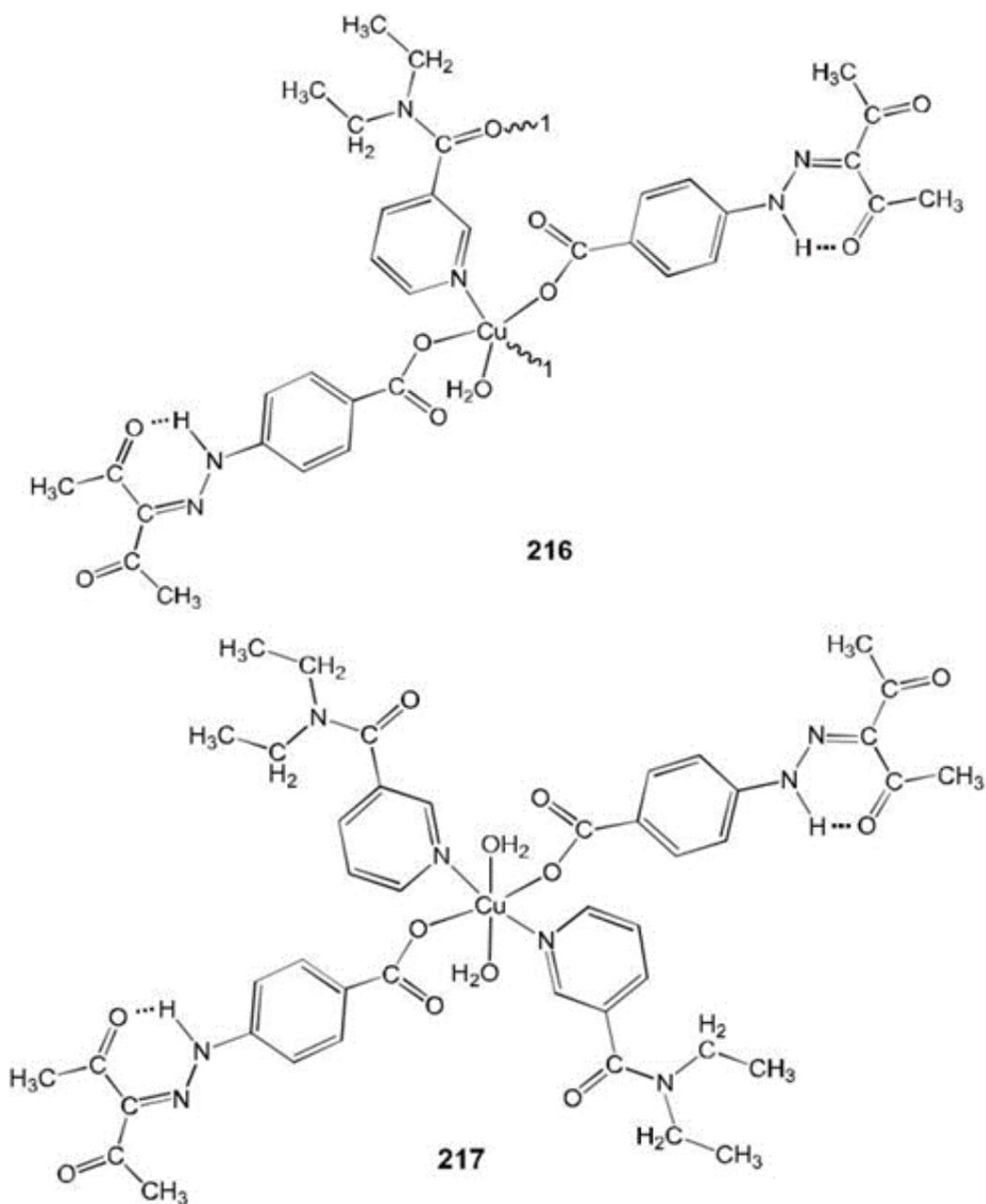


**Scheme 2.** Possible chelating modes of coordination within the AHBD complexes.





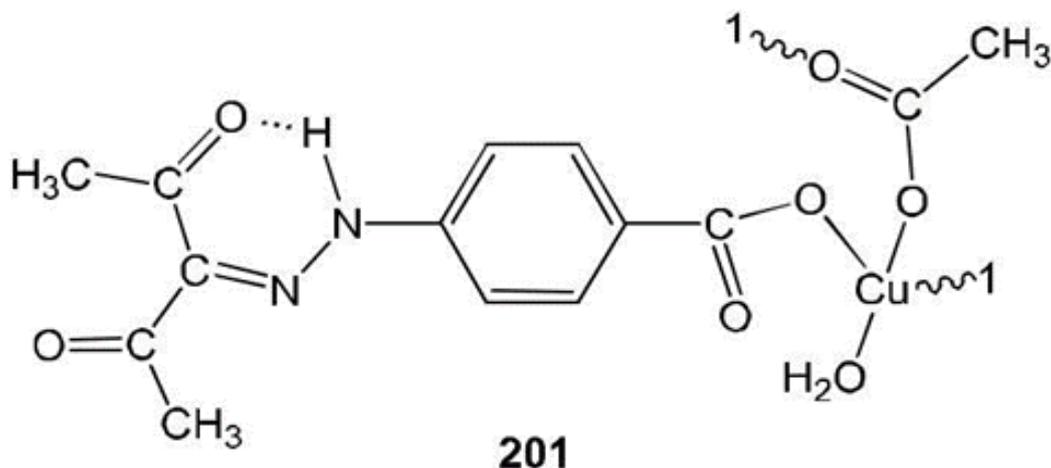
Scheme 6. Synthesis of AHMAC via RAHB.



Scheme 7. New copper (II) complexes 216 and 217.

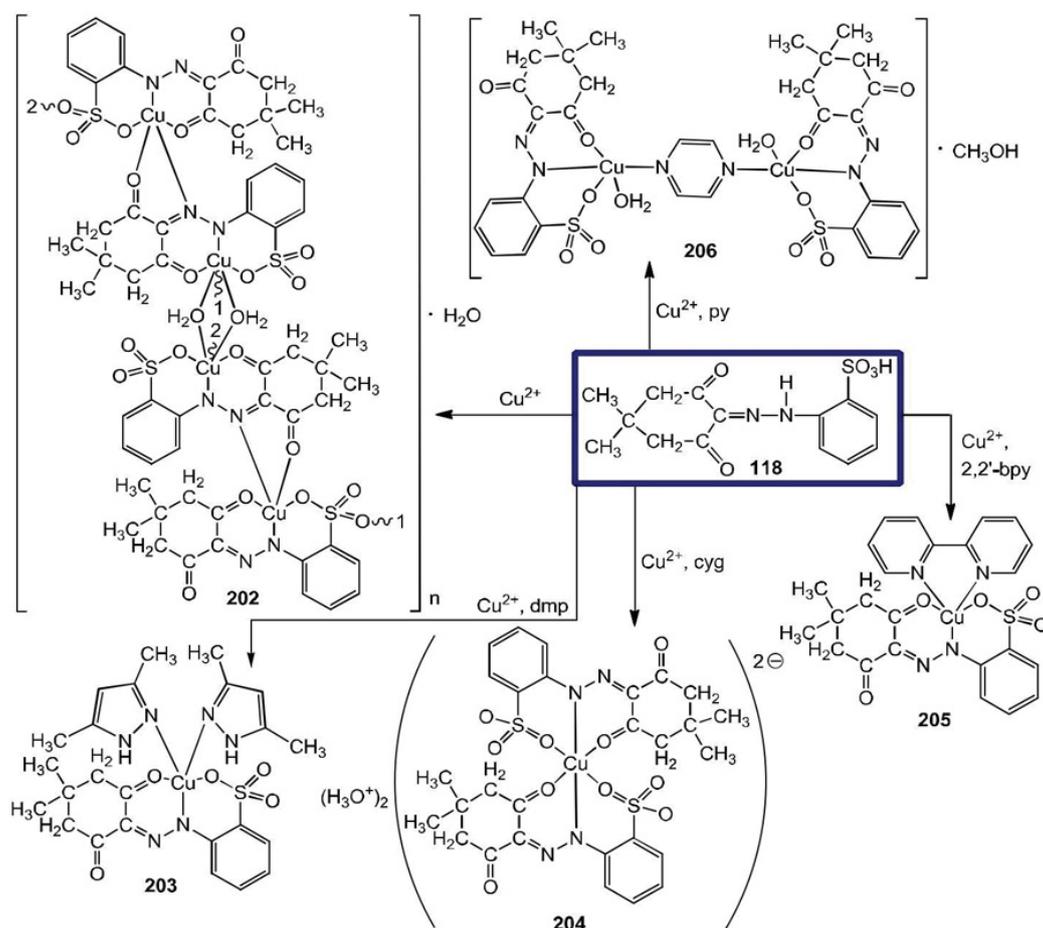
Kopylovich et al, prepared new copper (II) complexes 216 and 217 (**Schemes 5-8**) by reaction of copper II acetate hydrate with N,N-diethylpyridine-3- carboxamide (cardiamine) in the presence and absence of  $\text{Na}_2\text{CO}_3$ , respectively. The  $\text{Cu}^{\text{I}}$  atom in 216 exist in the plane defined by the oxygen atoms of the carboxylate ions, the nitrogen atom of pyridine moiety and the water molecule, while the apical coordination to the amido oxygen atom of an adjacent N-heterocycle leads to the polymeric chain formation.

Reaction of  $\text{Cu}^{\text{II}}$  acetate with 50 gave the polymer complex 201 (**Scheme 9**). The RAHB system stays intact and the  $\text{Cu}^{\text{II}}$  ions are complexed through coordination bonds by three carboxylate oxygen atoms from one AHBD ligand and two acetates.



**Scheme 8.** New copper (II) complexes 216 and 217.

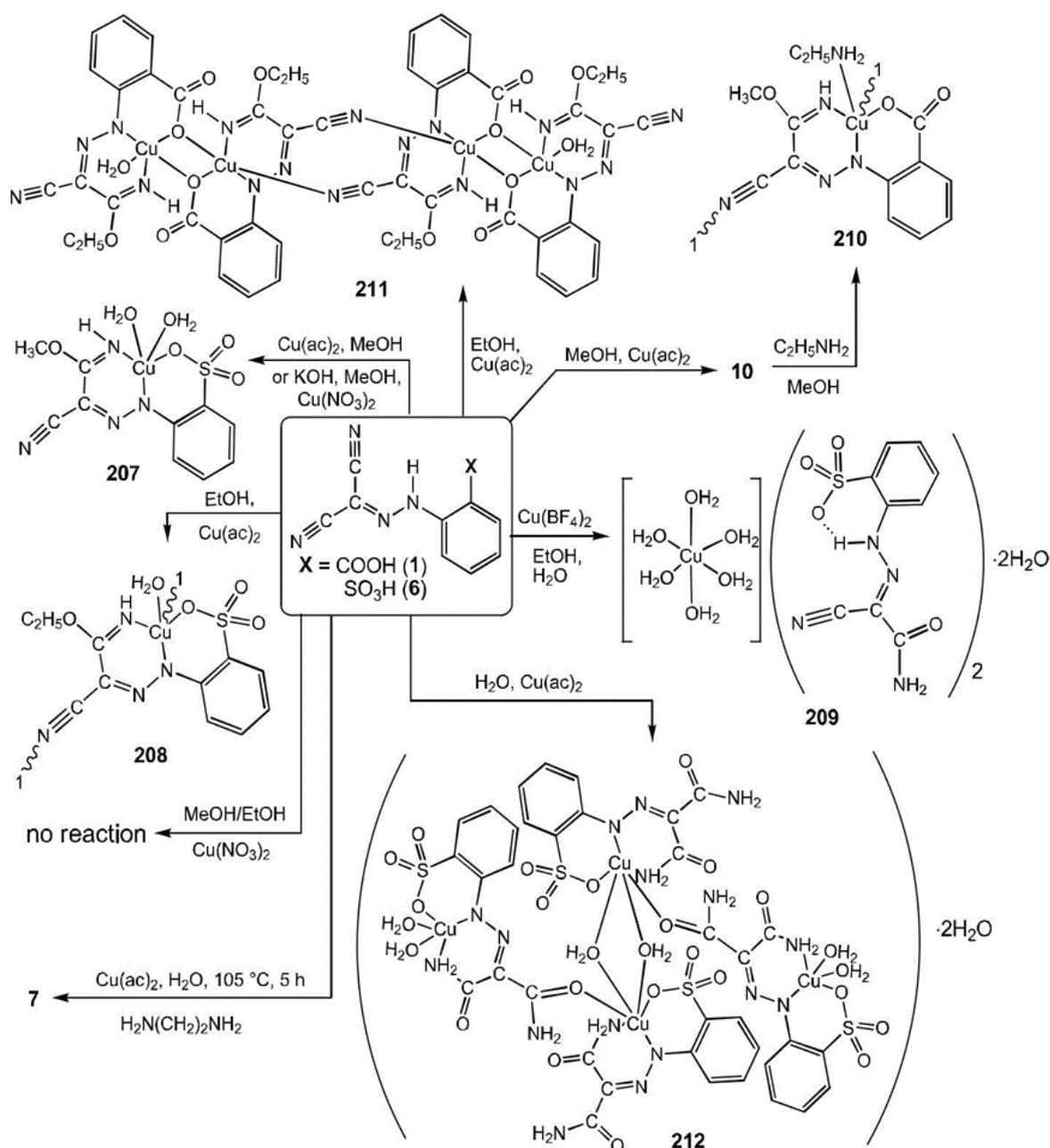
The  $\text{Cu}^{\text{II}}$ -AHBD complexes 202-206 were prepared by reacting 118 with a  $\text{Cu}^{\text{II}}$  source in the presence of auxiliary ligands (**Scheme 10**). In 202, water molecules act as bridges connecting two dimeric structural units, while a coordination polymer is formed by ligation of the sulfo- group to  $\text{Cu}^{\text{II}}$ . 202 is the first example in which both nitrogen atoms of the former hydrazone group are simultaneously coordinated to  $\text{Cu}^{\text{II}}$ . Pyrazine bridges two monomers forming 206. 202-206 were applied as catalysts in the oxidation of cyclohexane to cyclohexanol and cyclohexanone [21].



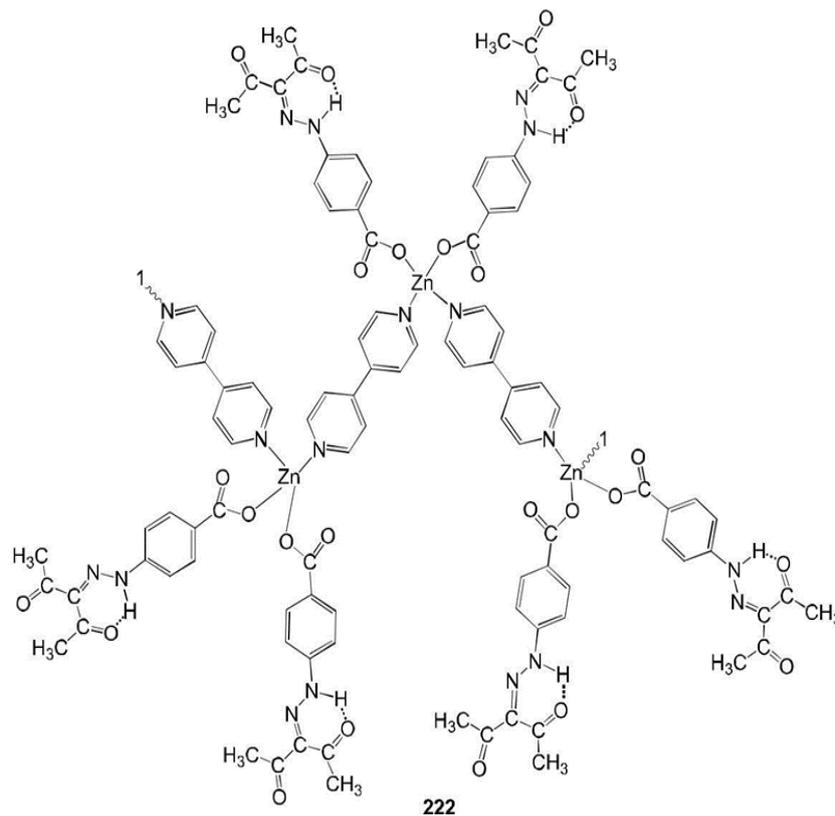
**Scheme 9.** AHBD complexes 202-206.

Kopylovich et al. studied the reactions of CuI with **1** and **6** in the presence of methyl alcohol, ethyl alcohol, water, ethylamine and ethylenediamine, nucleophilic attacks to the cyano moieties occur leading to a variety of different ligated amidines, carboxamides and iminoesters depending on the starting ligands, attacking nucleophiles, solvent and conditions used. Mononuclear **7**, **207-209**, tetranuclear **10**, **211**, **212** and polymeric **208** and **210** complexes were thus synthesized (**Scheme 11**) Selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds, as well as diastereoselective nitroaldol (Henry) reaction catalyzed by the complexes were studied, affording typical yields of 80-99%.

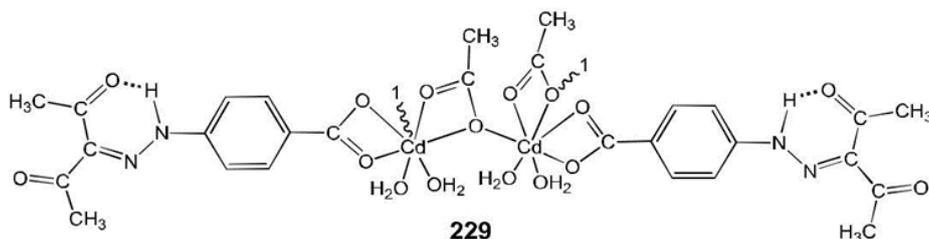
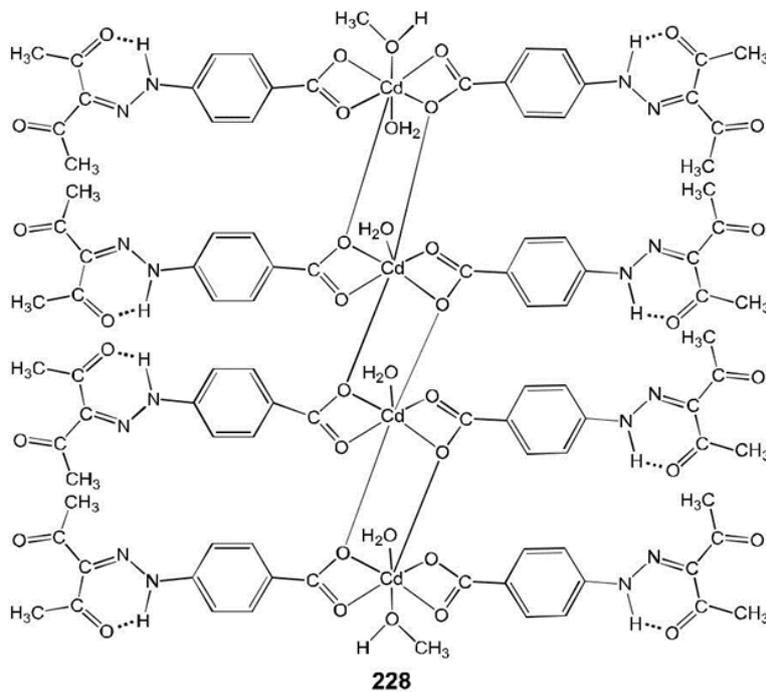
The coordination polymer **222** (**Scheme 12**) has been prepared by the reaction of the sodium salt of **50** with ZnII sulfate and 4,4'-bipyridine [22]. The ZnII ions are coordinated by two carboxylate oxygen atoms from two monodeprotonated **50** and two nitrogen atoms from two 4,4'-bipyridines. The metal ions are linked. Treatment of **50** with cadmium II nitrate and cadmium II acetate afforded complexes **228** and **229**, respectively [23,24]. In **228**, four CdII ions are bridged by bridging monodeprotonated **50** leading to a tetranuclear core. In the polymer **229**, the CH<sub>3</sub>COO<sup>-</sup> anions bridge the CdII ions forming 1D chain involving chelating monodeprotonated **50** units in the side chain. Each CdII atom is seven-coordinated, and is in a single-cap triangular prism environment with three oxygen atoms from two OOCCH<sub>3</sub> units, two oxygen atoms from one chelating **50** and two oxygen atoms from two water molecules. Thus, in the solid state structure of **229**, linear chains are bonded by intermolecular hydrogen bonds forming a 2D sheet. These 2D sheets were packed each other through Van der Waals forces forming a 3D supramolecular structure.



**Scheme 10.** Reactions of **1** and **6** with CuI.



**Scheme 11.** Freeman F Structures.



**Scheme 12.** Freeman F Structures.

## CONCLUSION

Arylhydrazones complexes have a great activity against different types of bacteria. They have been used in several of industrial synthetics of, e.g., herbicides, corrosion inhibitors, dyes, polymers, washing and bleaching compositions, catalysis, lubricants, and optical sensitizers and are widely utilized as azo dyes, PH-indicators, pigments, food additives, initiators for some radical reaction, therapeutic agents, etc. The coordination science of AACs has been extensively studied throughout the last decades on account of potential combination of important functional properties with a diversity of molecular structure of their complexes.

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