# Synthesis, molecular and crystal structure of bis-(2,4-bis(trichloromethyl)) triazapentadieneato-1,3,5 Cu(II) and Ni(II)

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#### Abstract

The reaction of thrichloroacetonitrile and NH<sub>4</sub>OH with participation of CuCl<sub>2</sub> and Ni(CH<sub>3</sub>COO)<sub>2</sub> leads to the corresponding complexes which are bis-(2,4-bis(trichloromethyl)) triazapentadieneato-1,3,5 Cu(II) and Ni(II). X-ray diffraction data showed that the metal atom in complexes is in an inversion center and possesses a square-planar coordination environment with two uninegatively charged 1,3,5-triazapentadienato chelators. In the solid state, the (N)H atoms of the ligands interact with oxygen atoms of solvent (CH<sub>3</sub>)<sub>2</sub>SO and (CH<sub>3</sub>)<sub>2</sub>NCHO to form six-membered intermolecular resonance assisted hydrogen bonding, while Cl atoms of the CCl<sub>3</sub> groups participate in Cl- - -Cl interactions thus generating 2D supramolecular assembly of distinctive geometry.

*Keywords:* template condensation, Ni(II) and Cu(II) tap complexes, resonance-assisted hydrogen bonding, Cl- - -Cl interactions.

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### **1. Introduction**

Recently we have studied catalytic olefination of terephthalic and metaphthalic aldehydes using trichloroacetonitrile. This reaction leads to desired products in moderate yields, which do not exceed 40 %. [1] Therefore, we decided to find more optimal reaction conditions and try to improve the yields of the desired products. For this purpose we studied various bases for the catalytic olefination (10 mol% of CuCl) of model hydrazone of 4-chlorobenzaldehyde **1** using aqueous ammonia, ethylenediamine, triethylamine, TMEDA and DBU (DMSO as a solvent). Surprisingly, no formation of 2-chloro-3-(4-chlorophenyl)-acrylonitrile **2** was observed when aqueous ammonia was used as the base. The reaction leads to formation of unexpected red crystalline product **3** (melting point 199-201° C) in 70-73 % yield. To establish the molecular and crystal structure of this compound we used X-ray diffraction. It turned out that copper chelate complex structures were formed in this reaction [2].

We believe that such unexpected reaction takes place due to increased electrophilicity of triple CN bond in trichloroacetonitrile. As a result addition of ammonia takes place to form

trichloracetamidine 4 as an intermediate. Being strong nucleophile compound 4 reacts with another molecule of trichloroacetonitrile to give intermediate 5 forming a copper chelate complex 3 - bis-(2,4-bi(trichloromethyl))-1,3,5-triazapentadieneato Cu(II). It should be noted that the trichloroacetonitrile (used in excess) acts as oxidizer towards copper chloride, transforming it into CuCl<sub>2</sub>. Crystals for X-ray analysis were obtained by slow crystallization of compound 3 from aqueous ethanol.



**Scheme 1.** Obtaining bis-(2.4-bis(trichloromethyl))1,3,5-triazapentadienato Cu<sup>II</sup> complex.



Figure 1. Molecular structure of the Cu (II) complex (a), the dashed lines show the intermolecular Cl-Cl bonds (b).

1,3,5-Triazapentadienes (tap) are isoelectronic analogs of  $\beta$ -diketones, which are very widely used in coordination chemistry [3]. Previously, a series of metal based tap were obtained and characterized. It should be noted that a number of compounds in this series have very interesting properties, such as spectral and exhibits high catalytic activity for certain reactions [4,5]. Recently a lot of attention was paid for the synthesis of tap complexes containing halogen atoms. Such compounds exhibit high thermal and chemical stability, specific volatility and high solubility in hydrocarbons. [6-21]. These complexes usually contain fluorinated substituents, currently only a few examples of chlorinated substituents are known, which typically refer to an aromatic series [6-13].

Complexes with halogenated ligands are frequently used in supramolecular chemistry as the fastening components with the ability to form hydrogen and halogen - halogen bonds. The relationship between halogens attracts attention as a tool for use in supramolecular chemistry, crystal engineering and other fields [22-24]. In view of these possibilities, we decided to develop new methods for the preparation of complexes based on other metals, based on tap system with trichloromethyl groups. These complexes could be of interest for supramolecular chemistry and to study halogen – halogen interactions.



Scheme 2. Probable mechanism of complex formation

As a result of experiments conducted with other complexing agents, in particular Ni, Pd, Zn, Pt, Fe, Co, Mn in various solvents (DMSO, DMF, alcohol) it was found that the reaction is general and proceeds in high yield. It was found that this reaction in DMSO and DMF flows with high speed and usually completes within 2-3 minutes. Experiments have shown an advantages of the developed method such as easiness of implementation (the reaction proceeds at room temperature without isolation of the intermediate formed ligands) cheapness of starting materials, high yields of the desired complex and its simple isolation from the reaction medium. [25-27].

$$CI_{3}C \longrightarrow NH_{3}, Me^{2+}, Me^{3+} Me[NH=C(CCI_{3})NC(CCI_{3})=NH]n$$

$$n=2 Cu, Ni, Zn, Pd$$

$$n=3 Fe, Mn, Co$$

This work is devoted to the study of the reaction with nickel salt in various solvents (DMSO, DMF, ethanol) as well as the preparation of copper complex in DMF medium. The obtained crystals were studied by X-ray to have a focus on molecular and crystalline structure of new tap complexes.

$$Cl_3C$$
 —  $CN + NH_3$    
 $a, b, c$    
 $Me\{NH=C(CCl_3)N=C(CCl_3)NH\}_2$   
 $1-4$   
 $Me = Ni, Cu$   $a = C_2H_5OH; b = DMSO; c = DMF$ 

Along with non-covalent bonds solvent molecules have been identified in the formation of crystals of complexes.



Figure 2. Molecular structures of complexes 1-4.



Figure 3. N-H ... O and CI ... CI bonds in the Cu (II) complex (1).



Figure 4. N-H ... O hydrogen and CI ... CI bonds in Ni (II) complex (2).



**Figure 5.** N-H … O hydrogen and N … CI bonds in Ni (II) complex (2).



Figure 6. N-H … O hydrogen and CI … CI bonds in Ni (II) complex (3)



Figure 7. Intermolecular and interlayer CI ... CI bonds in Ni (II) complex (4)

# 2. Experiments

## Synthesis of the complexes

1 mL water solution of 1.1 mmol of Ni(CH<sub>3</sub>COO)<sub>2</sub> was added to the mixture of 1.6 mL (11mmol) thrichloroacetonitrile and 2.5 mL (1M) of NH<sub>4</sub>OH in 20 mL DMSO and stirred for 10 min at ambient temperature giving orange precipitate of the product (6) which were filtered off and dried in air. The same process was performed in ethanol and DMF as solvents like in the case with DMSO and suitable orange (7,8) crystals were obtained. Similarly the reaction with CuCl<sub>2</sub> in DMF gave red crystals (9). The crystals suitable for X-ray structural analysis were obtained by recrystallization of 6-9 from C<sub>6</sub>H<sub>6</sub>:CH<sub>2</sub>Cl<sub>2</sub>.

{Ni[NH=C(CCl<sub>3</sub>)NC(CCl<sub>3</sub>)=NH]<sub>2</sub>}[(CH<sub>3</sub>)<sub>2</sub>SO]<sub>2</sub> (6): Yield 68 %; IR (KBr, selected bands, cm<sup>-1</sup>): 3244 and 3216 v(N-H), 1652 v(C=N), 1610  $\delta$ (NH). ESI-MS (in methanol): m/z 667 [M-2DMSOH]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>12</sub>H<sub>16</sub>Cl<sub>12</sub>N<sub>6</sub>NiO<sub>2</sub>S<sub>2</sub>, M = 824.55: C 17.48, H 1.96, N10.19; found: C 17.32, H 1.92, N10.03.

{Ni[NH=C(CCl<sub>3</sub>)NC(CCl<sub>3</sub>)=NH]<sub>2</sub>} (7): Yield 73 %; IR (KBr, selected bands, cm<sup>-1</sup>): 3244 and 3216 v(N-H), 1652 v(C=N), 1610  $\delta$ (NH). ESI-MS (in methanol): m/z 667. Elemental analysis calcd (%) for C<sub>8</sub>H<sub>4</sub>Cl<sub>12</sub>N<sub>6</sub>Ni, M = 668.60: C 14.38, H 0.60, N12.58; found: C 14.30, H 0.58, N12.42.

{Ni[NH=C(CCl<sub>3</sub>)NC(CCl<sub>3</sub>)=NH]<sub>2</sub>}[(CH<sub>3</sub>)<sub>2</sub>NCHO]<sub>2</sub> (8): Yield 74 %; IR (KBr, selected bands, cm<sup>-1</sup>): 3244 and 3216  $\nu$ (N-H), 1652  $\nu$ (C=N), 1610  $\delta$ (NH). ESI-MS (in methanol): m/z 667 [M-2DMFH]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>14</sub>H<sub>17</sub>Cl<sub>12</sub>N<sub>8</sub>NiO<sub>2</sub>, M = 813.42: C 20.70, H 1.99, N13.79; found: C 20.62, H 1.92, N13.64.

{Cu[NH=C(CCl<sub>3</sub>)NC(CCl<sub>3</sub>)=NH]<sub>2</sub>}[(CH<sub>3</sub>)<sub>2</sub>NCHO]<sub>2</sub> (9): Yield 70 %; IR (KBr, selected bands, cm<sup>-1</sup>): 3248 and 3224  $\nu$ (N-H), 1658  $\nu$ (C=N), 1609  $\delta$ (NH). ESI-MS (in methanol): m/z 672 [M-2DMSOH]<sup>+</sup>. Elemental analysis calcd (%) for C<sub>14</sub>H<sub>17</sub>Cl<sub>12</sub>N<sub>8</sub>CuO<sub>2</sub>, M = 818.28: C 20.57, H 1.97, N 13.71; found: C 20.44, H 1.92, N13.58.

# 3. Conclusion

Thus, we have synthesized and fully characterized a series of  $Cu^{II}$  and  $Ni^{II}$  tap complexes. In the complex, the central metal ion is coordinated in a rectangular-plane form with a monoanionic 1,3,5-triazapentadiene ligand, which acts as two N, N-chelates, forming two six-membered metal metallocycles. It was found that an intermolecular six-membered resonant auxiliary hydrogen bond is formed between the oxygen of the  $(CH_3)_2NCHO$  or  $(CH_3)_2S = O$  compounds and the (N)H part of the tap ligand. The formation of intermolecular  $CI \cdots N$ , halogen-halogen bonds depends on the solvent molecules used in the formation of the ensemble in  $M^{II}$ -tap-solvent complex. The complexes bind to each other by the interaction of strong hydrogen NH  $\cdots$  O, NH  $\cdots$  CI and halogen CI  $\cdots$  N, CI  $\cdots$  CI bonds and thus result in the formation of 2D supramolecular layers.

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