

SYNTHESIS AND INFRARED STUDY OF POLYNUCLEAR DABCO ADDUCTS WITH NiCl₂ AND CuCl₂

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Received: November, 03, 2014

Accepted: December, 18, 2014

Abstract: The proposed structures for the studied adducts - DABCO.3[NiCl₂·2H₂O].EtOH and 2DABCO.3CuCl₂.4EtOH or 3DABCO.4CuCl₂.5EtOH are discrete with two or three metallic components, the environments around the Nickel centres being octahedral or square planar, while being octahedral, linear or a square based prism around the Copper centres, the DABCO behaving as a monodentate or bridging bidentate ligand or being lattice. Extra intermolecular interactions via hydrogen bonds when considered, may lead to supramolecular architectures.

Keywords: monodentate, bidentate or lattice DABCO, polynuclear adducts with DABCO, octahedral, square planar or linear environments, supramolecular architectures

INTRODUCTION

The chemistry of 1,4-diazabicyclo [2, 2, 2]-octane (DABCO) has been widely visited [Cambridge data 2014]. Some MI_2 (M: Zn, Hg) DABCO adducts with a chain structure have been reported [1,2]; $M(CH_3CO_2)_2$ (M: Cd, Cu) [3,4], $InMe_3$ [5], $MgMe_2$ [6] and $ZnEt_2$ [7] adducts have also been reported, the DABCO behaving as a bridging bidentate ligand; adducts in which DABCO behaves as a monocoordinating ligand have also been reported [8-12]; only one DABCO adduct with $CuCl_2$ has been reported –very recently in 2013-[13] according Cambridge data. Because of the scarceness of data on DABCO adducts with $CuCl_2$ and $NiCl_2$, we have initiated in this work the study of the interactions between $CuCl_2$ and $NiCl_2 \cdot 6H_2O$ and DABCO which have yielded two new polynuclear adducts, infrared studies of which have been carried out then structures suggested on the basis of infrared data.

MATERIALS AND METHODS

Complexes **A**: $DABCO \cdot 3[NiCl_2 \cdot 2H_2O] \cdot EtOH$ and **B₁**: $2DABCO \cdot 3CuCl_2 \cdot 4EtOH$ or **B₂**: $3DABCO \cdot 4CuCl_2 \cdot 5EtOH$ were obtained on mixing the metal chloride (1eq) ($NiCl_2 \cdot 6H_2O$ or $CuCl_2$) with DABCO (2eq) in ethanol. The solution obtained when submitted to a slow solvent evaporation gives a dark brown powder for **A** and a brown one for **B**. The analytical data of the two compounds **A**, **B₁** and **B₂** are presented in Table 1.

Table 1. Results of the elemental analyses of compounds A, B₁ and B₂

Compound	Chemical formula	Elemental analysis (%)					
		C		H		N	
		calc.	found	calc.	found	calc.	found
A	$DABCO \cdot 3[NiCl_2 \cdot 2H_2O] \cdot EtOH$	14.66	14.11	4.58	3.11	4.27	4.35
B₁	$2DABCO \cdot 3CuCl_2 \cdot 4EtOH$	29.58	29.77	5.91	5.56	6.90	7.29
B₂	$3DABCO \cdot 4CuCl_2 \cdot 5EtOH$	29.48	29.77	6.14	5.56	7.37	7.29

The elemental analyses obtained and IR spectra performed on a Bruker FT-IR spectrometer from «Laboratoire de Mesures Physiques- Université de Montpellier II (France) ». Chemical reagents are purchased from ALDRICH Company (Germany).

RESULTS AND DISCUSSION

Let us consider the infrared data free DABCO and those of complexes **A** and **B**: Free DABCO [14].

IR data cm^{-1} : 2885; 1467; 1461; 1364; 1324; 1301; 1061; 1002; 910; 834; 783

A: $DABCO \cdot 3[NiCl_2 \cdot 2H_2O] \cdot EtOH$

IR data cm^{-1} : 3427.6; 3327.6; 2979.3; 1703.5; 1582.8; 1444.8; 1410.4; 1375.9; 1306.9; 1272.4; 1203.5; 1151.7; 1031; 893.1; 841.4; 789.7

B₁: 2 DABCO. 3 CuCl_2 .4 EtOH or **B₂**: 3 DABCO. 4 CuCl_2 .5 EtOH

B₁ and **B₂** IR data cm^{-1} : 3237.9; 3117.2; 3013.8; 1720.7; 1479.3; 1375.9; 1324.1; 1272.4; 1203.5; 1134.5; 1065.5; 996.1; 893.1; 858; 806; 737.9

On the infrared spectrum of **A** the presence of water molecules is correlated to the appearance of a broad band with minima at 3 427 and 3327 cm^{-1} due to ν_{as} H_2O and ν_{s} H_2O , this absorption being absent on the spectrum of **B**, **B** being an anhydrous compound.

The presence of only one molecule of EtOH in **A** and 4 or 5 molecules in **B** explains the broadness of the bands due to ν OH of EtOH in the spectrum of **B** allowing to assign the broad band at 3237 and 3013 cm^{-1} to ν OH and ν CH_2 of EtOH while the sharp and strong bands at 2979 cm^{-1} (**A**) and 3117 cm^{-1} (**B**) are due to ν CH_2 of DABCO. On the infrared spectrum of DABCO [14] ν CH_2 appears at 2885 cm^{-1} : the shift of ν CH_2 to higher frequencies in both (**A**) and (**B**) is due to the coordination of DABCO in these adducts.

Comparing $\nu_{\text{C}_3\text{N}}$ values of the free DABCO [14] with those of complexes DABCO shows a shift of $\nu_{\text{s}}\text{C}_3\text{N}$ and $\nu_{\text{as}}\text{C}_3\text{N}$ of DABCO in **A** and **B**- $\nu_{\text{as}}\text{C}_3\text{N}$ shifts to 1031(**A**) and 1065 (**B**) while $\nu_{\text{s}}\text{C}_3\text{N}$ shifts to 789 (**A**) and 806 (**B**). The shift of all those bands compared to those of free DABCO allows to consider a strong interaction between DABCO and the remaining parts of the complexes **A** and **B**.

A: DABCO. 3 $[\text{NiCl}_2 \cdot 2\text{H}_2\text{O}]$.EtOH

The shift of bands due to ν_{as} and ν_{s} NC_3 allows to consider the coordination through nitrogen. Considering the existence of the dimer of $[\text{NiCl}_2 \cdot 3\text{H}_2\text{O}]_2$ [15] we can therefore reasonably suggest a first structure which is a two metallic components, one of the components being the dimer above, the second metallic component being one $\text{NiCl}_2 \cdot \text{EtOH}$. DABCO: the structure is reported on Figure 1a.

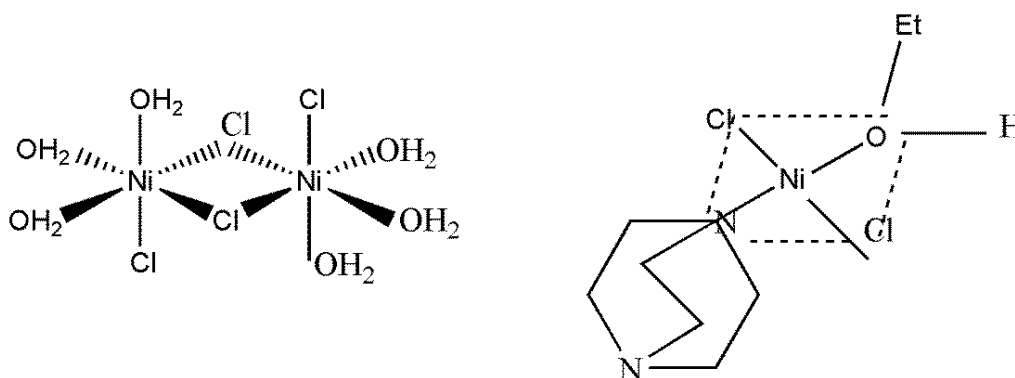


Figure 1a. Proposed structure for **A**

In terms of Ligand Field Theory, the tetrahedral environment of Ni in the second metallic component is not possible because of the coordinating power of DABCO and EtOH ligands. So the second metallic component is necessarily square planar (some interactions between the components cannot be excluded).

Considering the dimerization of the studied adduct, the rearrangement will give three metallic components: $[\text{Ni}_3\text{Cl}_{12}]^{6-}$, $[\text{Ni}_2(\text{H}_2\text{O})_{10}]^{4+}$ and $[\text{Ni}(\text{H}_2\text{O})_2(\text{EtOH})_2(\text{DABCO})_2]$.

The metallic component $[\text{Ni}_3\text{Cl}_{12}]^{6-}$ has been reported by Gerdes and Bond [16], the metallic component $[\text{Ni}_2(\text{H}_2\text{O})_{10}]^{4+}$ by Zhu and al [17] while the neutral metallic component containing three ligands every one twice occupying the opposite positions of an octahedron is similar to $[\text{DABCO.HSCN.SCN}]_2\text{Co}^{\text{II}}$, $[\text{DABCO.SCN.H}_2\text{O}]_2\text{Ni}^{\text{II}}$

DABCO, DMSO reported respectively by Cheng and al [10], Petrusenko and al [18]. The suggested structure is reported on Figure 1b the three metallic components interacting electro statically or through hydrogen bonds leading to a supramolecular architecture.

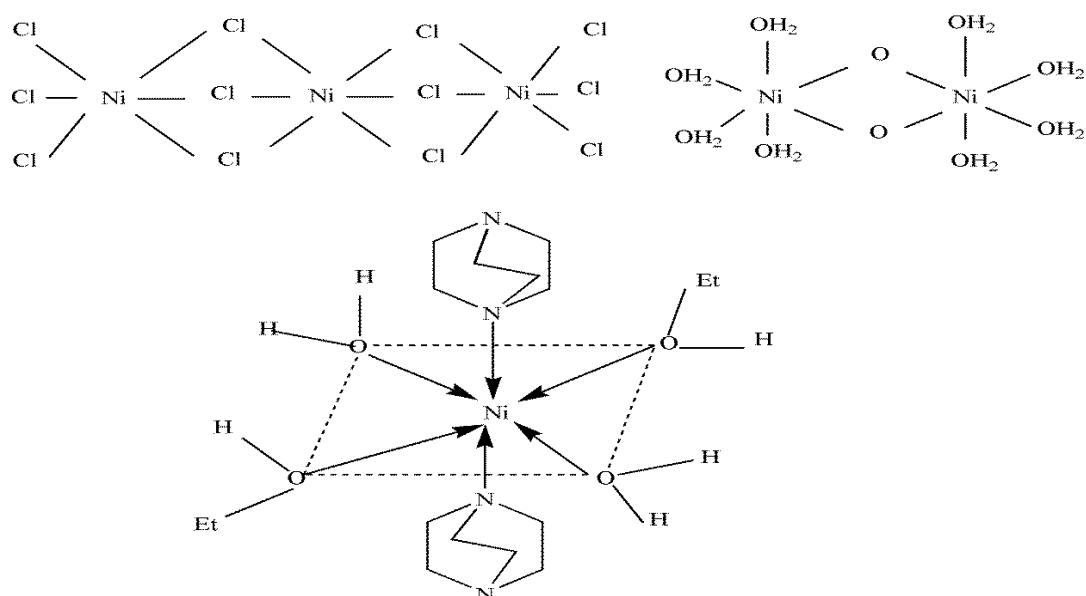


Figure 1b. Proposed structure for A

B₁: 2DABCO.3CuCl₂.4EtOH (29.58, 5.91, 6.90) or **B₂**: 3DABCO.4CuCl₂.5EtOH (29.48, 6.14, 7.37) (found: 29.77, 5.56, 7.29).

According to the elemental analyses the second formula sounds better while the first one cannot be definitely excluded. So we will consider both and suggest a structure for every molecule.

For commodity we will call the first adduct [2.3.4] and the second [3.4.5].

A first hypothesis allows considering [2.3.4] as [Cu₂Cl₆][Cu(EtOH)₄.DABCO] but according to the Cambridge Data no compound containing the frame work «Cu(EtOH)₄» exists allowing to reject this hypothesis.

We can consider two metallic components CuCl₂(EtOH)₂.DABCO in a square based pyramid arrangement interacting with CuCl₂ leading to the structure reported on Figure 2a.

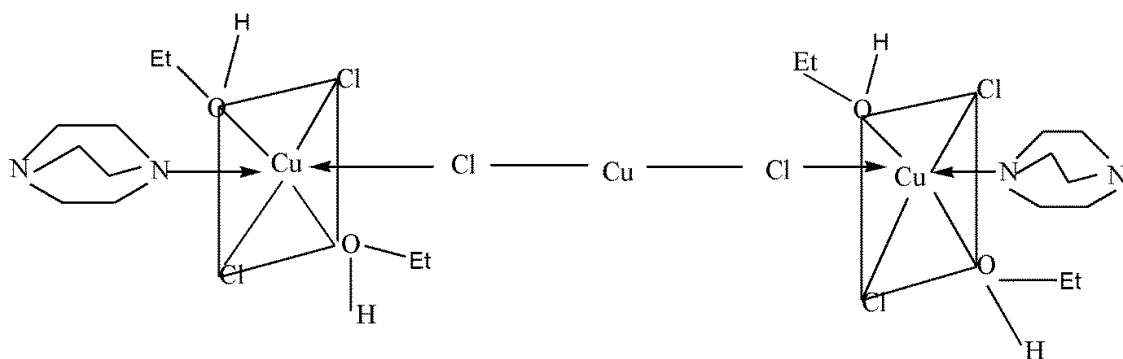


Figure 2a. Proposed structure for B₁

Or a central Cu^{2+} interacting with two octahedral $\text{CuCl}_3(\text{EtOH})_2\text{DABCO}$ leading to the structure reported on Figure 2b.

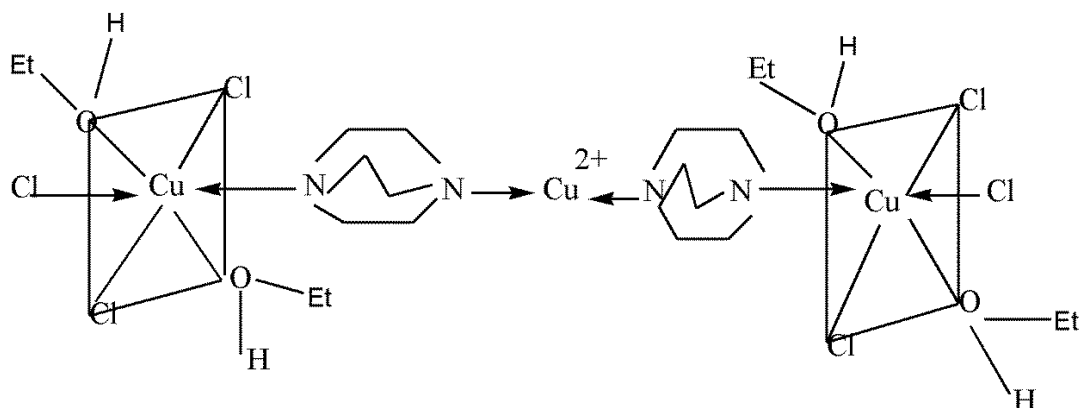


Figure 2b. Proposed structure for B_1

For [3.4.5] we can suggest the presence of $[\text{Cu}_3\text{Cl}_8.2\text{EtOH}]$ because of the existence of $[\text{Cu}_3\text{Cl}_8.2\text{H}_2\text{O}]^{2-}$ [19], the second metallic component being $[\text{Cu}(\text{EtOH})_3(\text{DABCO})_2]\text{DABCO}$, the last DABCO molecule being lattice because of steric factors. The suggested structure is reported on Figure 3.

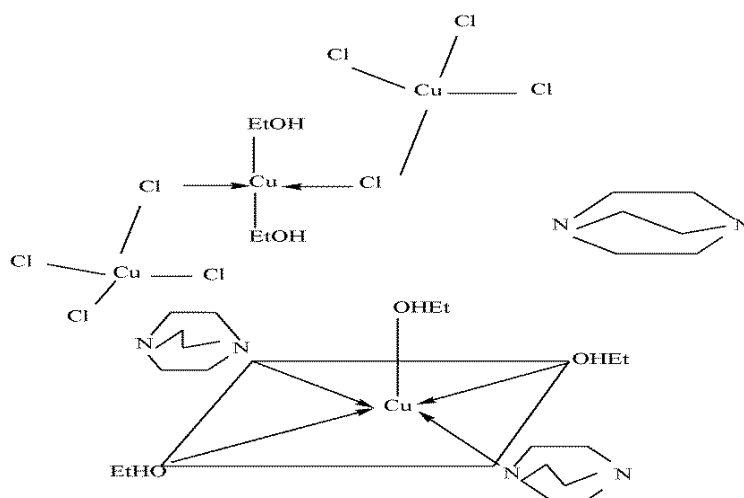


Figure 3. Proposed structure for B_2

CONCLUSION

Two components and three components structures have been suggested for Nickel studied adducts the environments around the Ni centres being square planar, octahedral or trigonal bipyramidal, the DABCO being a monocoordinating ligand while the Cu adduct has a discrete structure with linear and octahedral environments around the Cu centres, DABCO being a monocoordinating or a bridging bidentate ligand. In the various structures when extra interactions as hydrogen bonds are considered, supramolecular architectures are obtained.

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