

## INTERACTIONS BETWEEN CETYLTRIMETHYLAMMONIUM OR TETRAMETHYLAMMONIUM BROMIDE AND $MCl_2$ OR $MCl_5$ ( $M = Hg, Cu, Zn, Co, Ni, Cd$ and $Nb$ ) IN MONONUCLEAR COMPLEXES: SYNTHESIS AND INFRARED STUDY

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**Abstract:** On allowing cetyltrimethyl ammonium bromide ( $C_{19}H_{42}NBr$ ) and  $HgCl_2$ ,  $CuCl_2 \cdot 2H_2O$ ,  $CoCl_2 \cdot 6H_2O$ ,  $ZnCl_2$ ,  $NiCl_2 \cdot 6H_2O$  or  $NbCl_5$  in specific ratio in methanol, new mononuclear have been obtained and studied by infrared. The suggested structures are discrete, of infinite chain with octahedral or tetrahedral environments around the metallic centres. The  $MX_2$  behaves as discrete chains. For most of the structures, when intermolecular hydrogen bonds are considered, supramolecular architectures may be obtained.

**Keywords:** intermolecular hydrogen bonds, discrete structures, infinite chain, supramolecular architecture

### 1. INTRODUCTION

The interactions between transitional metal halide  $MX_2$  with alkylammonium halides have widely been studied by several worldwide groups because of their numerous physical properties [1-5]. In the case of copper (II), tetranuclear compounds  $Cu_4OX_6L_4$  or  $Cu_4O_4L_4X_4$  (X is a halide, L is a ligand) have been published [6-10]; catalytic properties of the cubane compound have been reported [11, 12]. During several decades our group has studied the coordinating power of oxyanions towards  $MX_2$  molecules [13-15].

In this dynamic, we have initiated in this work the study of the interactions between cetyltrimethyl ammonium bromide (CTAB) and some  $MCl_2$  molecules. This has yielded ten new adducts whose infrared study has been carried out then structures suggested based on infrared data.

### 2. MATERIALS AND METHODS

All the studied compounds have been obtained as white powders after a slow solvent evaporation at room temperature on allowing  $C_{19}H_{42}NBr$  or  $Bu_4NI$  to react in methanol with  $HgCl_2$  in 1:1 (**A**) and 1:2 (**B**) ratios,  $CoCl_2 \cdot 6H_2O$  in 2:1 ratio (**C**),  $ZnCl_2$  in 1:2 (**D**) ratio,  $NiCl_2 \cdot 6H_2O$  in 1:1 (**E**) and 1:2 (**J**) ratios,  $CuCl_2 \cdot 2H_2O$  in 2:1 ratio (**F**),  $NbCl_5$  in 1:1 (**G**), 1:2 (**H**) and 2:1 (**I**) ratios.

The mixtures were stirred around two hours before being submitted to a slow solvent evaporation.

The analytical data [% calculated (% found)], have allowed to suggest the following formulae (Table 1).

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Infrared spectra were recorded on a Bruker Vector 22 spectrometer equipped with a Specac Golden Gate™ ATR device. Infrared data are given in  $\text{cm}^{-1}$  [IR abbreviations: (vs) very strong, (s) strong, (m) medium, (vw) very weak].

Elemental analyses were performed at the “Institut de Chimie Moléculaire”, University of Bourgundy, Dijon (France). All chemicals were purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and used without any further purification.

Table 1. Results of the elemental analyses of compounds A-I.

Compound	Chemical formula	Elemental analysis [%]					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
<b>A</b>	$(\text{C}_{19}\text{H}_{42}\text{N})\cdot\text{HgBr}_3$	30.61	30.46	6.44	6.20	1.88	1.93
<b>B</b>	$(\text{Bu}_4\text{N})\cdot\text{HgI}_3$	27.94	28.70	5.23	3.988	2.04	2.15
<b>C</b>	$(\text{C}_{19}\text{H}_{42}\text{N})_2\cdot\text{CoCl}_3\text{Br}$	56.57	56.46	12.33	12.32	3.45	3.44
<b>D</b>	$(\text{C}_{19}\text{H}_{42}\text{N})_2\cdot\text{ZnBr}_3\text{Cl}$	51.54	51.26	11.57	11.22	3.13	3.08
<b>E</b>	$(\text{C}_{19}\text{H}_{42}\text{N})\cdot\text{NiBr}_3(\text{H}_2\text{O})_3\cdot 7\text{H}_2\text{O}$	36.6	36.22	9.733	8.89	2.26	2.22
<b>F</b>	$(\text{C}_{19}\text{H}_{42}\text{N})_2\cdot\text{CuBr}_2(\text{H}_2\text{O})_4\cdot\text{CuCl}_4(\text{H}_2\text{O})_2$	49.04	49.16	10.54	10.36	3.01	3.05
<b>G</b>	$(\text{C}_{19}\text{H}_{42}\text{NBr})_2\cdot\text{NbCl}_3\text{O}\cdot 2\text{H}_2\text{O}$	46.56	46.56	9.05	10.49	2.82	2.85
<b>H</b>	$(\text{C}_{19}\text{H}_{42}\text{NBr})\cdot\text{NbBr}_3\text{O}\cdot 2\text{H}_2\text{O}$	30.46	29.25	6.19	6.32	1.87	1.64
<b>I</b>	$(\text{C}_{19}\text{H}_{42}\text{NBr})_2\cdot\text{NbCl}_3\text{O}\cdot\text{H}_2\text{O}$	47.43	46.56	9.01	10.42	2.91	2.85

### 3. RESULTS AND DISCUSSION

#### 3.1. Compounds obtained with $\text{MCl}_2$ moiety

Let us consider the main IR data (Table 2) of compounds A-E.

Table 2. Main IR data of compounds A-E.

Complexes	N ( $\text{CH}_3$ and $\text{CH}_2$ )	$\nu$ ( $\text{NC}_4$ )	vas ( $\text{CH}_3$ and $\text{CH}_2$ )	$\nu$ (C-C)	$\rho$ ( $\text{CH}_2$ )
<b>A</b>	2923 (vs) 2854 (s)	911 (s)	1471 (s)	956	720 (m)
<b>B</b>	2922 (vs) 2854 (s)	912 (s)	1473 (s)	963	720 (m)
<b>C</b>	2921 (vs) 2855 (s)	912 (s) 907 (s)	1473 (s)	962	719 (m)
<b>D</b>	2922 (vs) 2854 (s)	911 (s)	1473 (s)	956	713 (m)
<b>E</b>	2921 (vs) 2854 (s)	912 (s)	1473 (s)	965	719 (m)

In the compounds **A-E** halide substitutions occur since the starting metallic chemicals are chlorinated.

From these infrared data, we have suggested:

- For **A** and **B**, while looking to the complex-anion  $[\text{HgBr}_3]^-$  or  $[\text{HgI}_3]^-$  which interacts electrostatically with the cation (cetyltrimethyl ammonium for **A** and tetrabutyl ammonium for **B**), a discrete monomeric structure (Fig. 1a) with an  $\text{Hg}^{\text{II}}$  centre linked to three bromides, the environment around the metallic centre being trigonal. A dimer, with two internal bridging bromides and two external ones on each mercury centre, have also been suggested (Figure 1b).

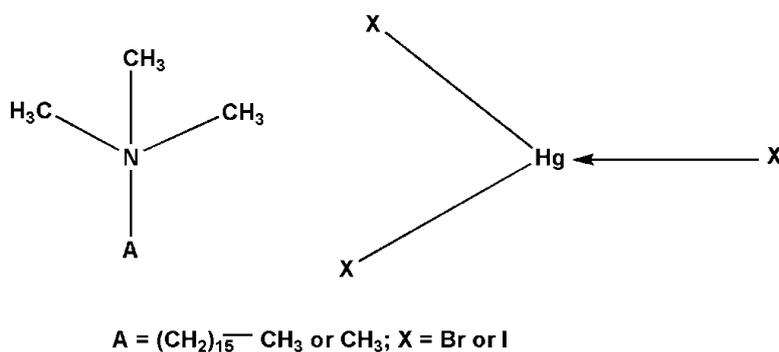


Fig. 1. a. Suggested structure for the compounds A and B.

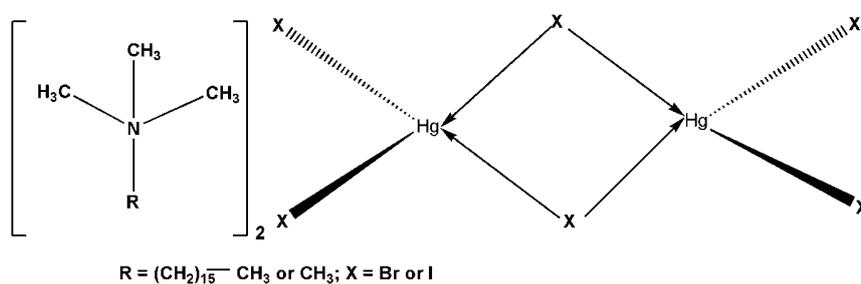


Fig. 1.b. Suggested structure for compounds A and B.

- For **C** and **D** while considering the complex-anion  $[\text{CoCl}_3\text{Br}]^{2-}$  or  $[\text{CoBr}_3\text{Cl}]^{2-}$ , a discrete structure with a metallic centre bonded to three chlorine atoms and one bromine atom or, to three bromine atoms and one chlorine atom, in a tetrahedral manner (Figure 2).

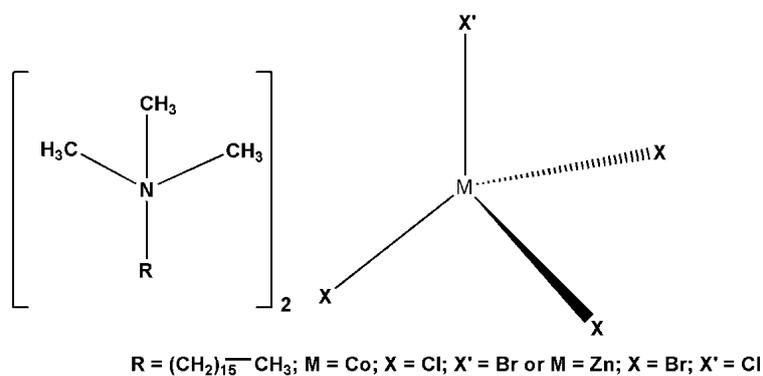


Fig. 2. Suggested structure for compounds C and D.

- For **E** while considering the complex-anion  $[\text{NiBr}_3(\text{H}_2\text{O})_3]^-$ , a discrete structure in which the  $\text{Ni}^{\text{II}}$  centre is linked to three bromides and three water molecules to complete the octahedral arrangement around the nickel centre, the remaining water molecules being lattice Figure 3.

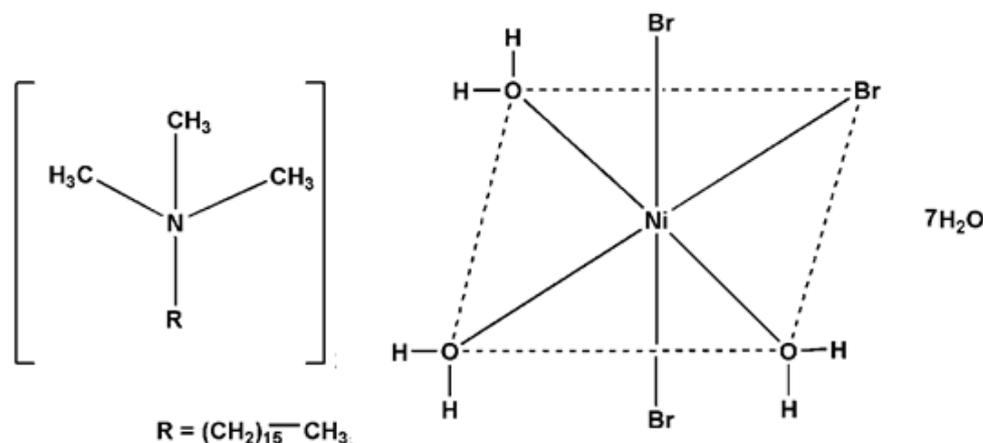


Fig. 3. Suggested structure for compound E.

- For **F**, a two metallic components: the first one being the molecule  $\text{CuCl}_2(\text{H}_2\text{O})_4$  whose metallic centre is in the middle of an octahedron, the second one being the complex-anion  $[\text{CuCl}_4(\text{H}_2\text{O})_2]^{2-}$  deriving from the previous molecule by replacing two water molecules with two chlorides (Figure 4).

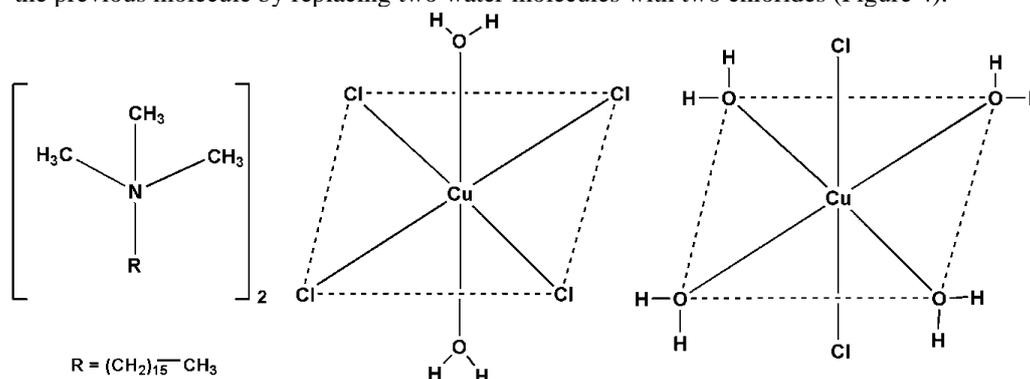


Fig. 4. Suggested structure for compound F.

### 3.2. Compounds obtained with $\text{MX}_3$ moiety

Let us consider the main IR data (Table 3) of compounds **G-I**.

Table 3. Main IR data of compounds G-I.

Complexes	$\nu$ ( $\text{CH}_3$ and $\text{CH}_2$ )	$\nu$ ( $\text{NC}_4$ )	vas ( $\text{CH}_3$ and $\text{CH}_2$ )	$\nu$ (C-C)	$\rho$ ( $\text{CH}_2$ )
<b>G</b>	2923 (vs) 2855 (s)	912 (s)	1474 (s)	961	717 (m)
<b>H</b>	2923 (vs) 2849 (s)	912 (s)	1474 (s)	962	718 (m)
<b>I</b>	2923 (vs) 2849 (s)	912 (s)	1474 (s)	961	718 (m)

It is noteworthy to outline that in these compounds the starting material  $\text{NbCl}_5$ , in its interactions with the CTAB turn into  $\text{NbCl}_3\text{O}$  or into  $\text{NbBr}_3\text{O}$ . From these infrared data we suggest:

- For **G**, and **H** a discrete structure consisting of a  $\text{NbX}_3\text{O}$  ( $X = \text{Cl}$  or  $\text{Br}$ ) molecule on which two water molecules come set, the metallic centre being seven coordinated (Fig. 5).

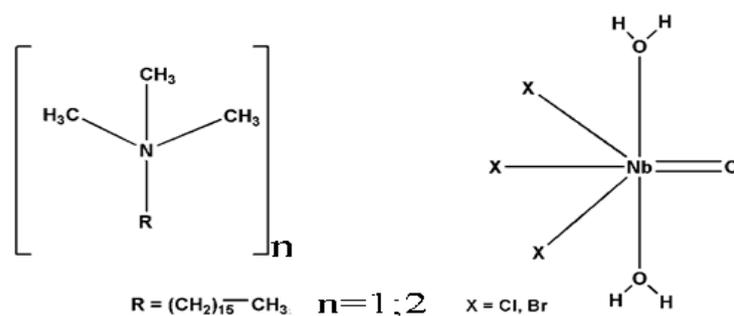


Fig. 5. Suggested structure for compounds G, and H.

- For **I** a discrete structure coming the previous one by removing one water molecule, the Nb centre being six coordinated (Figure 6).

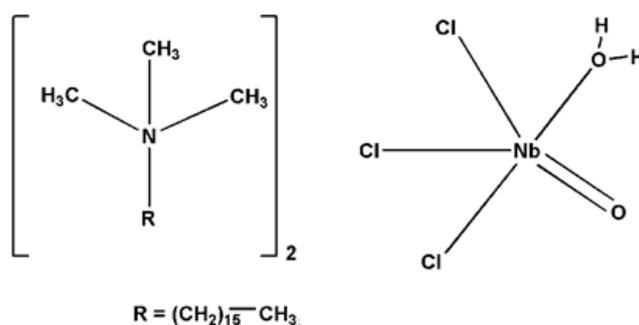


Fig. 6. Suggested structure for compound I.

#### 4. CONCLUSION

With the CTAB cation we have been able to obtain simple structures with complex tetrahedral or octahedral ions. The transformation of  $\text{NbCl}_5$  in  $\text{NbCl}_3\text{O}$  or  $\text{NbBr}_3\text{O}$  was found in the study of interactions involving  $\text{NbCl}_5$ .

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