INTERACTIONS BETWEEN CETYLTRIMETHYLAMMONIUM OR TETRAMETYLEAMMNONIUM BROMIDE AND MCl₂ OR MCl₅ (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 (C₁₉H₄₂NBr) and HgCl₂, CuCl₂.2H₂O, CoCl₂.6H₂O, ZnCl₂, NiCl₂.6H₂O or NbCl₅ 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 MX₂ 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 MX₂ 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), tetrannuclear compounds Cu₄OX₄L₄ or Cu₄OₓLₓX₄ (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 MX₂ molecules [13-15].

In this dynamic, we have initiated in this work the study of the interactions between cetyltrimethyl ammonium bromide (CTAB) and some MCl₂ 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 C₁₉H₄₂NBr or Bu₄NI to react in methanol with HgCl₂ in 1:1 (A) and 1:2 (B) ratios, CoCl₂.6H₂O in 2:1 ratio (C), ZnCl₂ in 1:2 (D) ratio, NiCl₂.6H₂O in 1:1 (E) and 1:2 (J) ratios, CuCl₂.2H₂O in 2:1 ratio (F), NbCl₅ 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 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 |
| A        | (C₁₉H₄₂N)HgBr₃  | 30.61 | 30.46 | 6.44  | 6.20  | 1.88  | 1.93  |
| B        | (Bu₄N)HgI₃      | 27.94 | 28.70 | 5.23  | 3.988 | 2.04  | 2.15  |
| C        | (C₁₉H₄₂N)₂CoCl₂Br | 56.57 | 56.46 | 12.33 | 12.32 | 3.45  | 3.44  |
| D        | (C₁₉H₄₂N)₂ZnBr₂Cl | 51.54 | 51.26 | 11.57 | 11.22 | 3.13  | 3.08  |
| E        | (C₁₉H₄₂N)₂NiBr₂(H₂O)₃.7H₂O | 36.6 | 36.22 | 9.733 | 8.89 | 2.26  | 2.22  |
| F        | (C₁₉H₄₂N)₂CuBr₂(H₂O)₄.CuCl₂(H₂O)₂ | 49.04 | 49.16 | 10.54 | 10.36 | 3.01  | 3.05  |
| G        | (C₁₉H₄₂NBr)₂.NaCl₂.H₂O | 46.56 | 46.56 | 9.05  | 10.49 | 2.82  | 2.85  |
| H        | (C₁₉H₄₂NBr)₂.NbBr₂.O₂H₂O | 30.46 | 29.25 | 6.19  | 6.32  | 1.87  | 1.64  |
| I        | (C₁₉H₄₂NBr)₂.NbCl₂.O₂H₂O | 47.43 | 46.56 | 9.01  | 10.42 | 2.91  | 2.85  |

### 3. RESULTS AND DISCUSSION

#### 3.1. Compounds obtained with MCl₂ 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 (CH₃ and CH₂) | ν (N≡C) | ν as (CH₃ and CH₂) | ν (C-C) | ρ (CH₂) |
|-----------|----------------|---------|------------------|---------|---------|
| A         | 2923 (vs) 2854 (s) | 911 (s) | 1471 (s) | 956 | 720 (m) |
| B         | 2922 (vs) 2854 (s) | 912 (s) | 1473 (s) | 963 | 720 (m) |
| C         | 2921 (vs) 2855 (s) | 912 (s) 907 (s) | 1473 (s) | 962 | 719 (m) |
| D         | 2922 (vs) 2854 (s) | 911 (s) | 1473 (s) | 956 | 713 (m) |
| E         | 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 [HgBr₃]⁻ or [HgI₃]⁻ which interacts electrostatically with the cation (cetyltrimethyl ammonium for A and tetrabutyl ammonium for B), a discrete monomeric structure (Fig. 1a) with an Hg^{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).
For C and D while considering the complex-anion [CoCl\(_3\)Br\(_2\)]\(^{-}\) or [CoBr\(_3\)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).

For E while considering the complex-anion [NiBr\(_3\)(H\(_2\)O)\(_3\)]\(^{-}\), a discrete structure in which the Ni\(^{II}\) 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 CuCl$_2$(H$_2$O)$_2$ whose metallic centre is in the middle of an octahedron, the second one being the complex-anion [CuCl$_4$(H$_2$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 MX$_3$ moiety

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

| Complexes | $\nu$ (CH$_3$ and CH$_2$) | $\nu$ (NC$_4$) | vas (CH$_3$ and CH$_2$) | $\nu$ (C-C) | $\rho$ (CH$_2$) |
|-----------|--------------------------|---------------|------------------------|-------------|--------------|
| G         | 2923 (vs)                | 912 (s)       | 1474 (s)               | 961         | 717 (m)      |
|           | 2855 (s)                |               |                        |             |              |
| H         | 2923 (vs)                | 912 (s)       | 1474 (s)               | 962         | 718 (m)      |
|           | 2849 (s)                |               |                        |             |              |
| I         | 2923 (vs)                | 912 (s)       | 1474 (s)               | 961         | 718 (m)      |
|           | 2849 (s)                |               |                        |             |              |

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

- For G, and H a discrete structure consisting of a NbX$_3$O (X = Cl or Br) molecule on which two water molecules come set, the metallic centre being seven coordinated (Fig. 5).
- For I a discrete structure coming the previous one by removing one water molecule, the Nb centre being six coordinated (Figure 6).

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

**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 NbCl$_5$ in NbCl$_3$O or NbBr$_3$O was found in the study of interactions involving NbCl$_3$.

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