

NEW ADDUCTS BETWEEN N-[FERROCENYLMETHYL] DIMETHYLAMMONIUM AND HALOMETALLATES: SYNTHESIS AND INFRARED STUDY

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Received: July, 01, 2015

Accepted: November, 10, 2015

Abstract: Eight new adducts between N-[ferrocenylmethyl]dimethylammonium and halometallates were obtained in ethanolic media. From an infrared study, the suggested structures are monomeric or dimeric for tin compounds which contain $[\text{SnCl}_4(\text{OH})_2]^{2-}$, $[(\text{SnCl}_5)]^-$ and $[(\text{SnI}_5)]^-$, $[\text{SnCl}_3(\text{OH})_2]^-$ and $[(\text{SnI}_6)]^{2-}$ complex anions, interacting through hydrogen bonds with the cation, the environments around tin (IV) centers being trigonal bipyramidal or octahedral. For hydrated Cu(II) and Cd(II) adducts, we proposed dimeric structures with hydrogen bridges between cation and water H_2O , the environments around Cu(II) being trigonal and trigonal bipyramidal, respective octahedral around Cd(II). One of the compounds may contain the hydrogen bis [N-ferrocenylmethyldimethylamine] captive cation with a hydrogen bond (N-H...N), the cation interacting electrostatically with $[\text{ZnBr}_4]^{2-}$. The crucial role of the cation in all the compounds is outlined. The molecules of cyclopentadiene obtained *in situ* are lattice.

Keywords: polyhalostannic - chlorocuprates - chlorocadmate and bromozincate species, trigonal bipyramidal, tetrahedral, trigonal or octahedral environments

INTRODUCTION

Among the possible *N*-[ferrocenylmethyl]dimethylammonium halometallates, only the structure of *N*-[ferrocenylmethyl]dimethylammonium tetrachlorozincate monohydrate was reported [1], but the structures of *N*-[ferrocenylmethyl]dimethylammonium salts like halides (Cl^- , Br^- , I^-), nitrate or hydrogen oxalate [2 – 6] are well known. Because of the absence of such data on tin and for enhancing the data on MX_2 molecules we have initiated here the study of the interactions between slightly hydrated *N*-[ferrocenylmethyl]dimethylamine and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, SnI_4 , CuCl_2 , CdCl_2 and ZnBr_2 , which has yielded the eight studied adducts; infrared study of which has been carried out, then probable structures were suggested on the basis of infrared data.

MATERIALS AND METHODS

The studied adducts have been obtained on mixing hydrated *N*-[ferrocenylmethyl]dimethylamine (L) with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, SnI_4 , CuCl_2 , CdCl_2 and ZnBr_2 in various ratios. All the mixtures give a clear solution; a powder is obtained after a slow solvent evaporation. The following compounds were obtained for specific ratio L/metal halide:

- L + $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 2:1 ratio gives (**A**) as a yellow powder;
- L + $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1:1 ratio gives (**B**) as a green powder;
- L + SnI_4 in 2:1 ratio gives (**C**) as a yellow-orange powder;
- L + CuCl_2 in 1:1 ratio gives (**D**) as a light green powder;
- L + CuCl_2 in 2:1 ratio gives (**E**) as a yellow green powder;
- L + CuCl_2 in 1:2 ratio gives (**F**) as a dark green powder;
- L + CdCl_2 in 2:1 ratio gives (**G**) as a beige powder;
- L + ZnBr_2 in 2:1 ratio gives (**H**) as a beige powder.

The analytical data reported below have allowed to suggest the following formulae for the eight new adducts (Table 1):

Table 1. Suggested formulae of the synthesized compounds

| Comp | Suggested formulae | Chemical composition [% mass] | | | | | |
|----------|---|-------------------------------|-------|-------|-------|-------|-------|
| | | C | | H | | N | |
| | | Calc. | Found | Calc. | Found | Calc. | Found |
| A | $[\text{SnCl}_4(\text{OH})_2][\text{NFeMD}]_2 \cdot \text{H}_2\text{O}$ | 36.13 | 36.23 | 4.37 | 4.31 | 2.87 | 2.92 |
| B | $[\text{SnCl}_6][\text{SnCl}_5][\text{NFeMD}]_3 \cdot 2\text{H}_2\text{O} \cdot \text{C}_5\text{H}_6$ | 38.11 | 38.13 | 5.12 | 5.30 | 3.42 | 3.45 |
| C | $[\text{SnI}_7][\text{NFeMD}]_3 \cdot \text{C}_5\text{H}_6 \cdot 1/4\text{FeCp}_2\text{CH}_2\text{NHMe}_2\text{OH}$ | 30.31 | 30.17 | 3.46 | 3.37 | 2.43 | 2.44 |
| D | $[\text{DMAMFeH}][\text{CuCl}_3] \cdot \text{H}_2\text{O}$ | 36.12 | 36.77 | 4.63 | 5.01 | 3.24 | 3.14 |
| E | $[\text{DMAMFeH}]_3[\text{CuCl}_5] \cdot 1/2 \text{C}_5\text{H}_6 \cdot \text{H}_2\text{O}$ | 48.66 | 48.93 | 5.70 | 5.93 | 4.10 | 3.90 |
| F | $[\text{DMAMFeH}][\text{Cu}_2\text{Cl}_5] \cdot 1/2 \text{EtOH} \cdot \text{H}_2\text{O}$ | 28.59 | 28.43 | 3.90 | 4.04 | 2.34 | 2.38 |
| G | $[\text{DMAMFeH}]_5[\text{CdCl}_7] \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ | 48.88 | 49.09 | 5.95 | 6.07 | 4.25 | 4.30 |
| H | $[(\text{Fe}(\text{Cp})_2\text{CH}_2\text{NMe}_2)_2\text{H}]_2[\text{ZnBr}_4] \cdot 2\text{C}_5\text{H}_6$ | 49.89 | 49.68 | 5.50 | 5.56 | 3.75 | 3.81 |

Elemental analyses and IR spectra, performed on a Bruker FT-IR spectrometer, have been obtained from the «Laboratoire de Mesures Physiques - Université de Montpellier II – France». Chemical reagents are purchased from ALDRICH Company (Germany) and used without any further purification.

RESULTS AND DISCUSSION

Let us consider the infrared data of complexes **A**, **B** and **C** in cm^{-1} :

A: $[\text{SnCl}_4(\text{OH})_2][\text{NFeMD}]_2 \cdot 2\text{H}_2\text{O}$: 758.73; 822.22; 853.97; 917.46; 949.21; 996.83; 1036.51; 1092.1; 1155.6; 1179.4; 1242.9; 1306.4; 1338.1; 1385.7; 1417.5; 1465.1; 1600; 1973; 2044.4; 2179.4; 2290.5; 2322.2; 2663.5; 2742.8; 2798.4; 3036.6; 3131.8; 3528.6; 3592.

B: $[\text{SnCl}_5][\text{SnCl}_6][\text{NFeMD}]_3 \cdot 2\text{H}_2\text{O} \cdot \text{C}_5\text{H}_6$: 838.1; 933.3; 949.2; 1028.6; 1052.4; 1076.2; 1115.9; 1131.85; 1171.43; 1242.9; 1290.5; 1385.71; 1401.6; 1465.1; 1568.3; 1980.9; 2060.3; 2163.5; 2361.9; 2465.1; 2512.7; 2560.32; 2949.21; 2965.51; 3092.1; 3369.84.

C: $[\text{SnI}_7][\text{NFeMD}]_3 \cdot \text{C}_5\text{H}_6 \cdot 1/4\text{NFeMDOH}$: 824.12; 927.6; 933.3; 996.5; 1016.7; 1048.24; 1100; 1255.2; 1290; 1393.1; 1453.4; 2332.74; 2393.1; 2703.44; 2927.6; 3099.96; 3410.

If we consider the infrared spectrum of ferrocene [7] there is no band between 820 and 1000 cm^{-1} . The appearance of bands at 928 cm^{-1} on the spectrum of (dimethylaminomethyl)ferrocene (DMAMFe) [8], respective at 948 and 922 cm^{-1} on the spectrum of $\text{DMAMFe} \cdot \text{HCl}$ allows to assigned these bands to $\nu(\text{NC}_3)$. The bands relative to NH , OH and H_2O appear as broad or intense bands (underlined bands) allowing to conclude to the presence of hydrogen bonds. For the compound **A** two structures has been proposed (Figure 1a and Figure 1b).

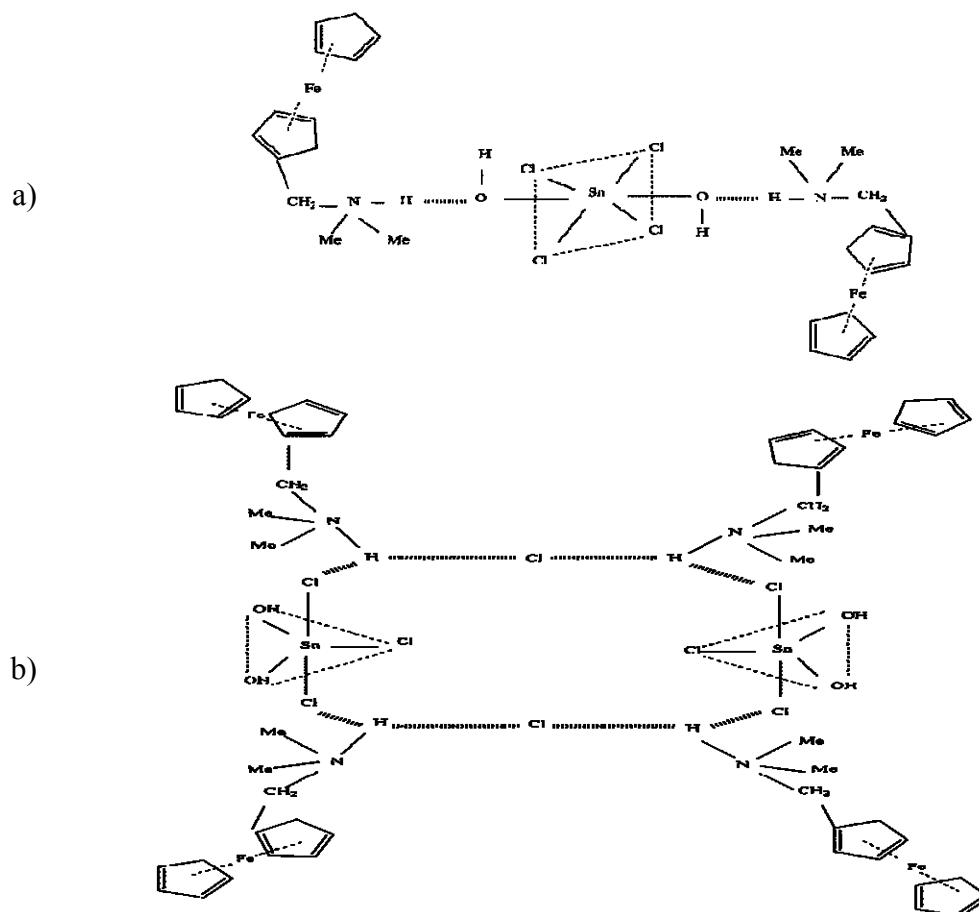


Figure 1. Proposed structures for **A**

The first suggested structure consists of octahedral $[\text{SnCl}_4(\text{OH})_2]^{2-}$ species linked through O atoms by hydrogen bonds to the cation (Figure 1a);

A second structure may be suggested, consisting of two $[\text{SnCl}_3(\text{OH})_2]^-$ moieties in a trigonal bipyramidal arrangement linked by cation... Cl^- ...cation strings (Figure 1b).

When the OH groups are involved in extra hydrogen bonds involving OH, H_2O and chloro atoms, a supramolecular architecture may be obtained.

The compound **B** contains two $[\text{SnCl}_5]^-$ species; these ones have yet been reported in [9], the environment around the tin center being trigonal bipyramidal. There are two suggested structures:

- the first one consists of a central chloride linked to three chloro atoms of the two $[\text{SnCl}_5]^-$ species by the three cations through $\text{NH}\cdots\text{Cl}$ bifurcated hydrogen bonds (Figure 2a).
- the second one consists of two $[\text{SnCl}_5]^-$ species linked by the chloro atoms in apical positions through one cation... Cl^- ...cation string or cation only (Figure 2b). The water and cyclopentadiene molecules may be considered as lattice ones.

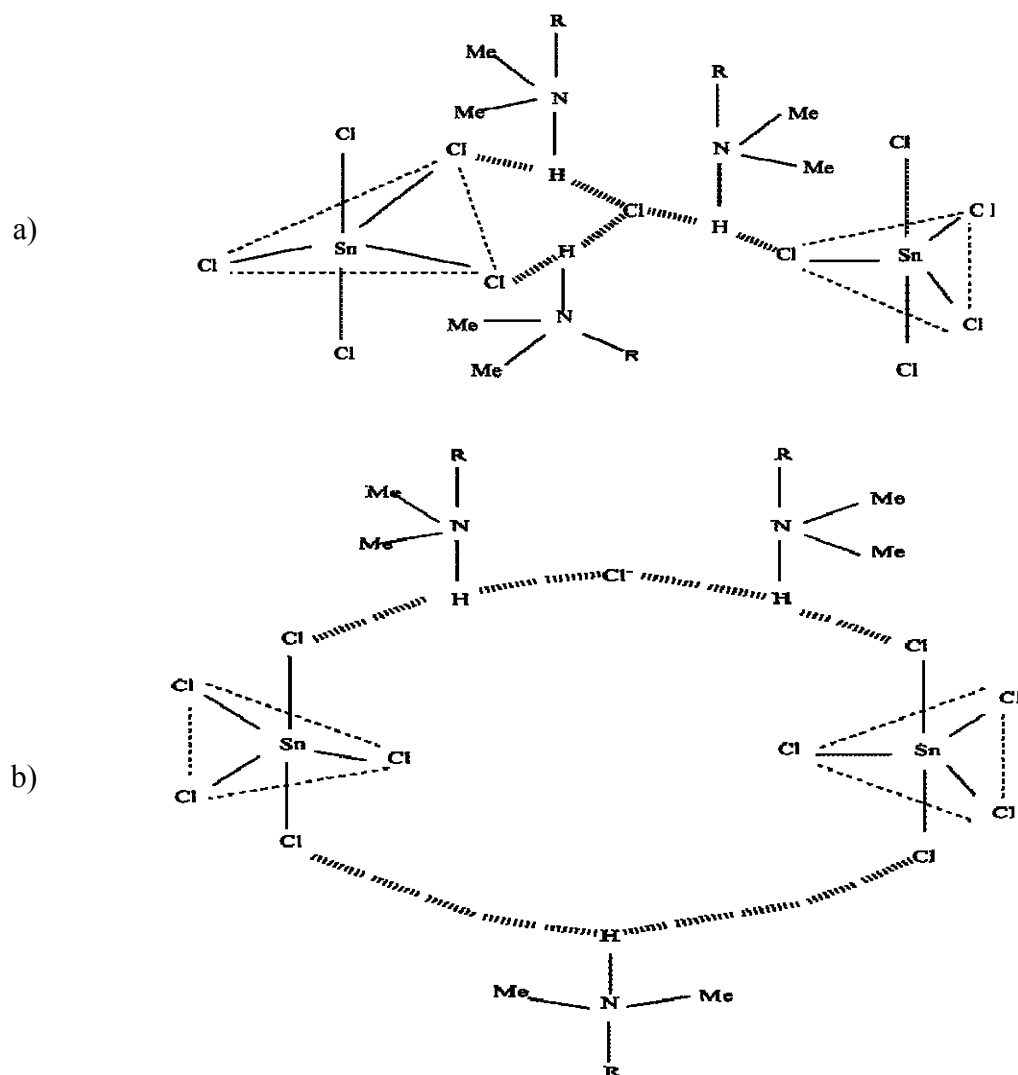


Figure 2. Proposed structures for **B** ($R = \text{CH}_2\text{FeCp}_2$)

While considering the complex-anion $[\text{SnI}_7]^{3-}$, visiting the Cambridge Data allow to conclude to the non-existence of such anion but only $[\text{SnI}_5]^-$ and $[\text{SnI}_6]^{2-}$ [10, 11]. For the compound **C** the two suggested structures consist of two $[\text{SnI}_5]^-$ species in a trigonal bipyramidal environment connected through hydrogen bonded strings of cation...I⁻.....cation.....I⁻.....cation type leading to the structure reported on Figure 3a or two $[\text{SnI}_6]^{2-}$ anions linked by cationI⁻.....cation string or cation only leading to the structure reported in Figure 3b (the cyclopentadiene molecules are lattice).

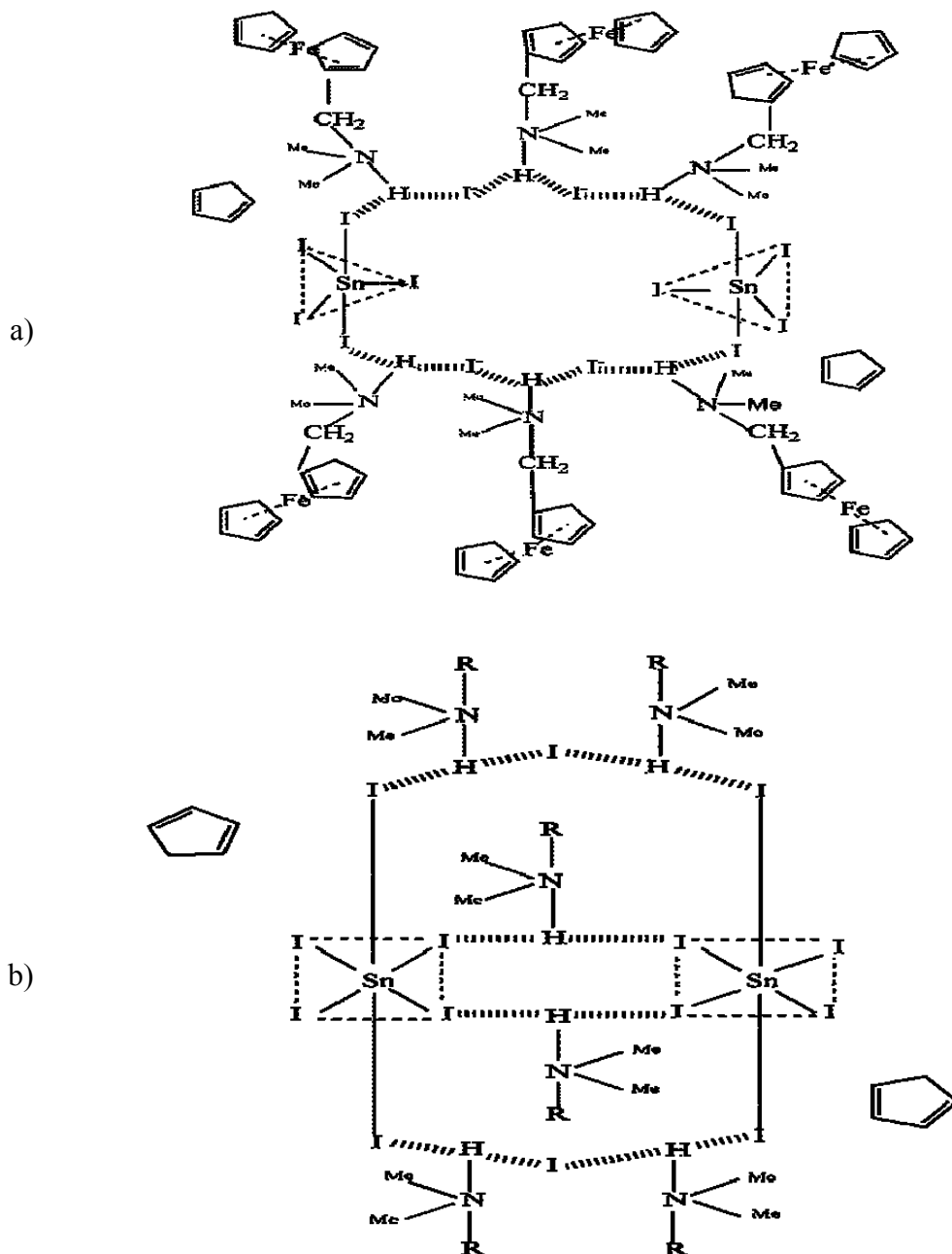


Figure 3. Proposed structures for **C**

Let us consider the infrared data of complexes **D**, **E**, **F**, and **G** in cm^{-1} :

D: $[\text{DMAMFeH}][\text{CuCl}_3] \cdot \text{H}_2\text{O}$: 910.3; 944.8; 996.6; 1108.6; 1292.3; 1410.8; 1479.3; 1591.34; 2151.72; 2358.6; 2668.96; 2944.8; 3350.

E: $[\text{DMAMFeH}]_3[\text{CuCl}_5] \cdot \frac{1}{2}\text{C}_5\text{H}_6 \cdot \text{H}_2\text{O}$: 727.4; 791.1; 836.6 ;912.5; 927.6; 939.34; 991.3; 1027.7; 1091.4; 1227.4; 1300.2; 1409.4; 1482.2; 1663.7; 1727.4; 2336.6; 2373; 2482.2; 2600; 2691; 2936.7; 3091.4; 3245.6; 3382.1.

F: $[\text{DMAMFeH}][\text{Cu}_2\text{Cl}_5] \cdot \frac{1}{2}\text{EtOH} \cdot \text{H}_2\text{O}$: 761.3; 806.35; 877.8; 933.3; 1035.5; 1100; 1147.62; 1306.4; 1385.7; 1481; 1592.1; 1742.9; 1965.1; 2179.4; 2278; 2798.4; 2997; 3330.2; 3433.3.

G: $[\text{DMAMFeH}]_5[\text{CdCl}_7] \cdot \text{EtOH} \cdot \text{H}_2\text{O}$: 808.8; 847.2; 917.3; 934; 1000.8; 1034.2; 1100; 1233.6; 1350.5; 1400.6; 1467.4; 1658.5; 2348.8; 2450.7; 2542.6; 2567.6; 2668.8; 2942.4; 3034.3; 3242; 3359.

The presence of bands due to $\nu(\text{NC}_3)$, $\nu(\text{N-H})$ and $\nu(\text{H}_2\text{O})$ (underlined bands) on the obtained spectra is the evidence of the presence of $\text{DMAMFe} \cdot \text{H}_2\text{O}$.

While considering $[\text{DMAMFeH}][\text{CuCl}_3] \cdot \text{H}_2\text{O}$ (**D**), $[\text{CuCl}_3]^-$ complex-anion has been trapped as a monomer in the adduct structure [12]. So having in mind the structure of bis[dimethylaminomethylferrocenium][ZnCl_4] $\cdot \text{H}_2\text{O}$, we can suggest for $[\text{DMAMFeH}][\text{CuCl}_3] \cdot \text{H}_2\text{O}$ a structure similar to the one of $[\text{DMAMFeH}]_2\text{ZnCl}_4 \cdot \text{H}_2\text{O}$, $[\text{CuCl}_3]^-$ replacing $[\text{ZnCl}_4]^{2-}$. The suggested structure for (**D**) is reported on Figure 4.

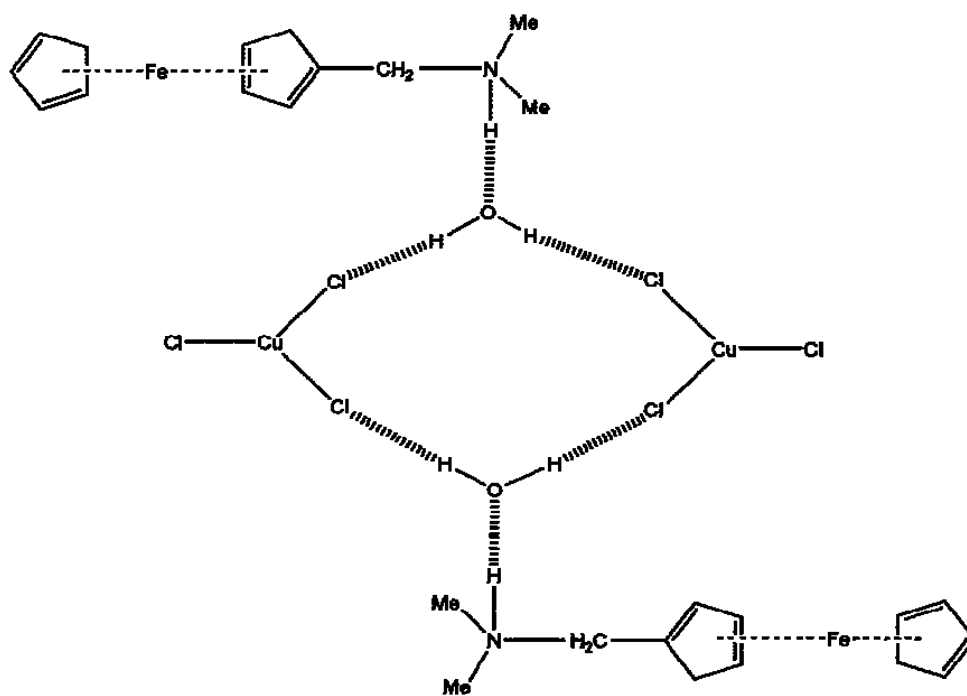


Figure 4. Proposed structure for **D**

Extra $\text{Cl} \cdots \text{Me}$ or $\text{Cl} \cdots \text{HC}$ hydrogen bonds may give a supramolecular architecture.

$[\text{DMAMFeH}]_3[\text{CuCl}_5] \cdot \frac{1}{2}\text{C}_5\text{H}_6 \cdot \text{H}_2\text{O}$ (**E**): $[\text{CuCl}_5]^{3-}$ is known as a monomer [13]; the structure as above is dimeric $[\text{CuCl}_5]^{3-}$ replacing $[\text{CuCl}_3]^-$, C_5H_6 being lattice. The suggested structure is reported on Figure 5.

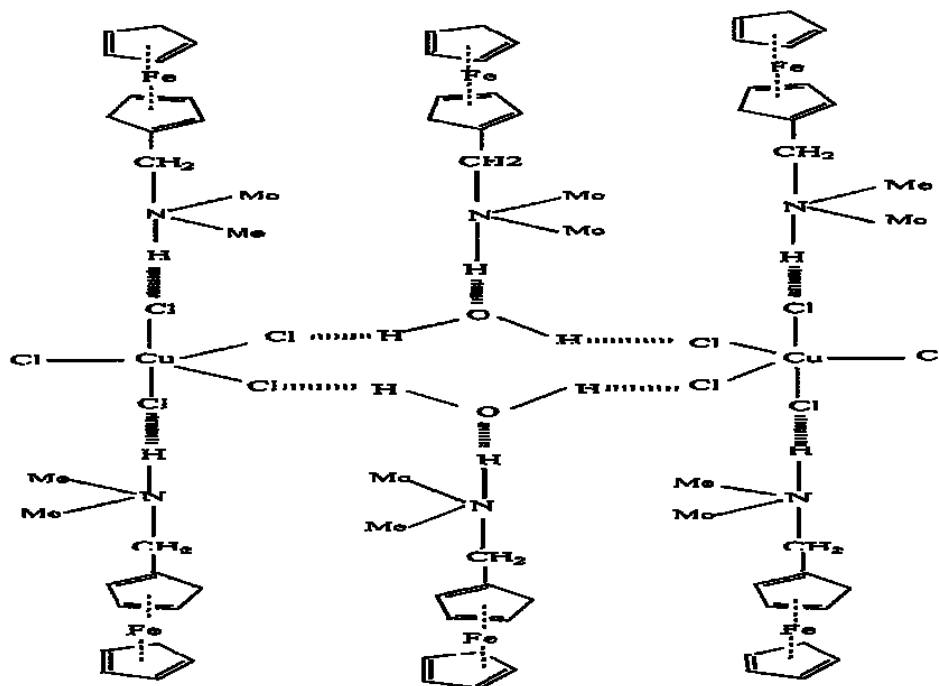


Figure 5. Proposed structure for *E*

For $[\text{DMAMFeH}][\text{Cu}_2\text{Cl}_5] \cdot \frac{1}{2}\text{EtOH} \cdot \text{H}_2\text{O}$ (**F**), $[\text{Cu}_2\text{Cl}_5]^-$ is known having a tridimensional structure [14]; however it seems reasonable to consider the cleavage of this structure into monomers. In this structure $[\text{Cu}_2\text{Cl}_5]^-$ replaces $[\text{CuCl}_3]^-$ in (**D**), EtOH being lattice. The suggested structure is reported on Figure 6.

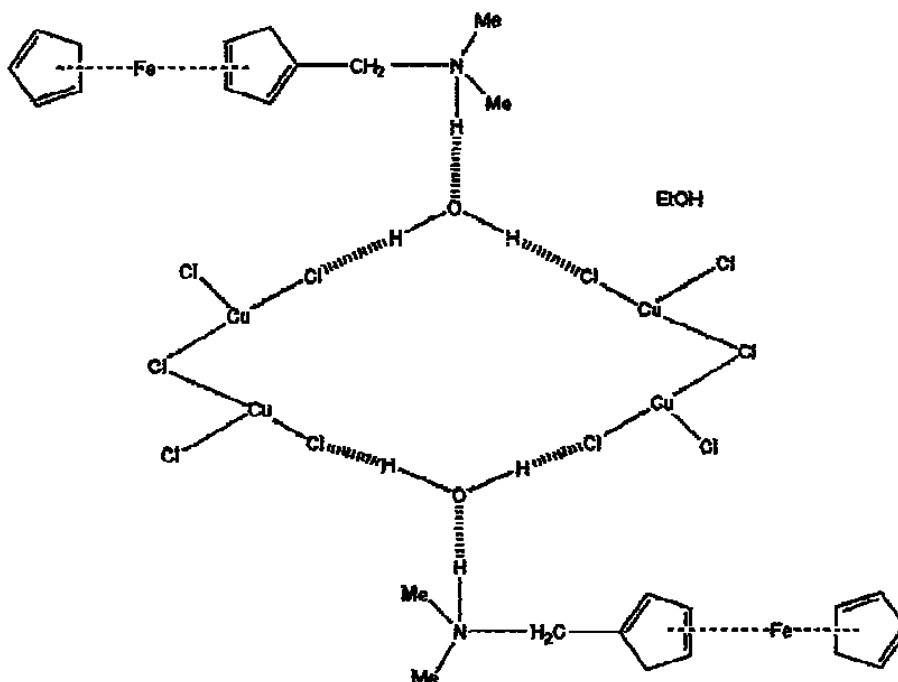


Figure 6. Proposed structure for *F*

For $[\text{DMAMFeH}]_5 \cdot \text{CdCl}_7$ (**G**) the anion $[\text{CdCl}_7]^{5-}$ has not yet been reported but $[\text{CdCl}_6]^{4-} \cdot 2\text{Cl}^- \cdot 2\text{H}_2\text{O}$ and $[\text{CdCl}_6]^{4-} \cdot 4\text{Cl}^-$ [15, 16] the coordination sphere receiving the six chlorides, the external 4Cl^- or 2Cl^- and $2\text{H}_2\text{O}$ interacting with the cation and the water molecules.

So this studied complex can be considered as $[\text{CdCl}_6]^{4-} \cdot \text{Cl}^-$ allowing to suggest the structure reported on Figure 7.

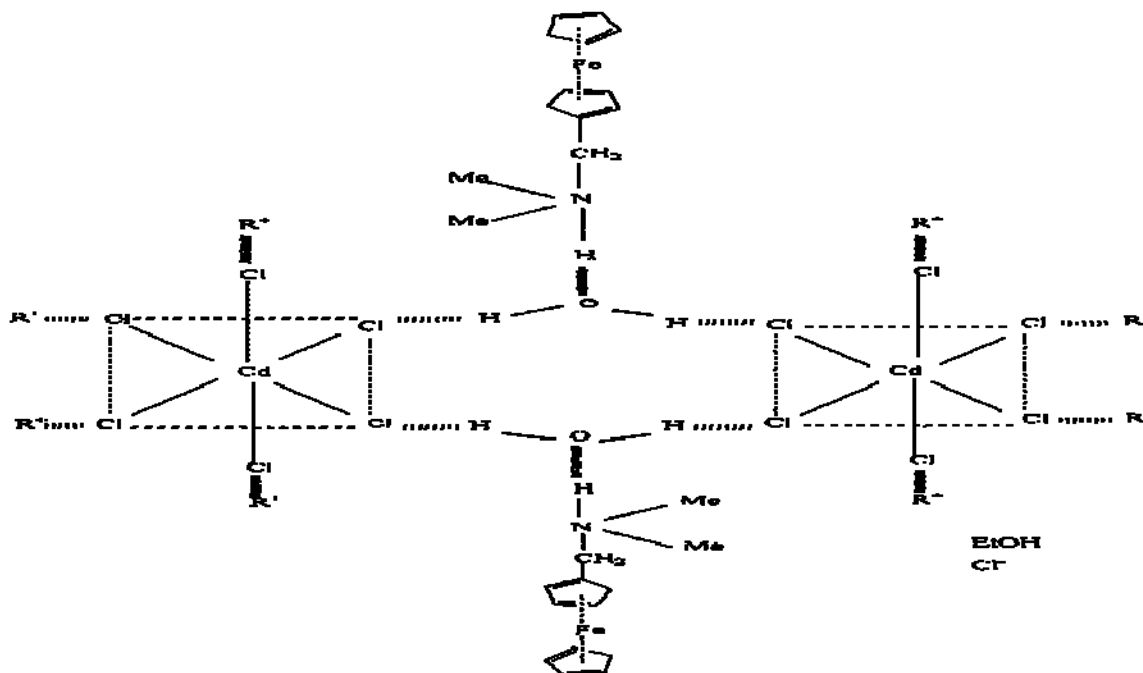


Figure 7. Proposed structure for **G** ($R = \text{NFeMDMA}$)

The remaining cations are connected to the chloro atoms through $\text{N-H} \cdots \text{Cl}$ hydrogen bonds as above on Figure 7, EtOH being lattice while the external Cl^- interact electrostatically with the positive components of the structure.

H: $[\text{NFeMDMA}]_2\text{ZnBr}_4 \cdot 2\text{C}_5\text{H}_6$: 734.9; 806.4; 835; 927.5; 977.8; 981; 1020.6; 1060.32; 1119.1; 1160.32; 1207.94; 1274.6; 1354; 1393.7; 1441.3; 1663.5; 1711.1; 2338.1; 2433.33; 2473.02; 2536.5; 2631.8; 2877.8; 2904.8; 2949.21; 3028.6.

The absorption centered at 2440 cm^{-1} on the spectrum of $\text{DMAMFe} \cdot \text{HCl}$ is due to $\nu(\text{N-H})$. The underlined bands 927.5 and 2631.8 are due to the cation DMAMFeH^+ .

The main specific feature of this spectrum is the broad band centered at 2631 cm^{-1} assigned to $\nu \text{ N-H} \cdots \text{N}$ hydrogen bond due to the presence of the captive cation $[(\text{FeCp}_2\text{CH}_2\text{NMe}_2)_2\text{H}]^+$, reported on Figure 8 with two captive cations interacting electrostatically with $[\text{ZnBr}_4]^{2-}$; the two molecules of cyclopentadiene are lattice. This type of structure had yet been reported with $[(\text{Bz}_3\text{O})_2\text{H}]^+$ ($\text{Bz} = \text{benzyl}$) as captive cation the complex-anion being $[\text{CuCl}_4]^-$ [17].

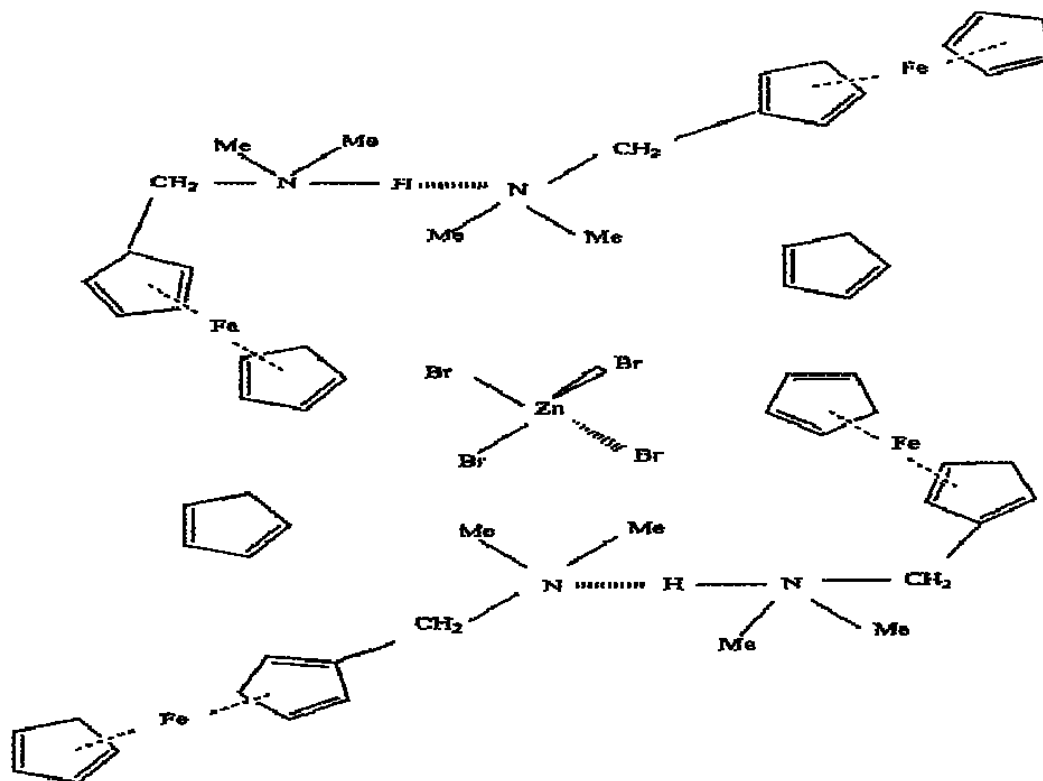


Figure 8. Proposed structure for *H*

CONCLUSIONS

We proposed for the studied compounds monomeric or dimeric structures, the environments around the Sn, Cu, Zn and Cd centers being octahedral or trigonal bipyramidal. In these studied adduct hydrogen bonded cation...X⁻...cation.....X⁻.....cation or cation...X⁻.....cation strings (X = Cl, I) ensure the dimerization. The four hydrated chlorometallates containing adducts studied have all dimeric structures with H₂O bridges ensuring the dimerization. In the bromozincate complex, the adverse cation is the captive cation [(FeCp₂CH₂NMe₂)₂H]⁺ which interacts electrostatically with the tetrabromozincate anion. The key role of the cation in all the structures is noteworthy. The cyclopentadiene molecules obtained in situ are lattice. In the suggested structures, extra C-H...Cl, Br or I hydrogen bonds, when possible, may connect the dimers and lead to a supramolecular architecture.

ACKNOWLEDGEMENTS

We deeply thank Dr. A. Manteghetti and Dr. Y. Euzet (University of Montpellier II - France) for the gift of SnI₄.

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