

**NEW TIN (IV), MX_2 AND $\text{M}'\text{Cl}_3$ ($\text{M} = \text{Zn, Hg}$; $\text{M}' = \text{Pr, Er}$)
ADDUCTS AND COMPLEXES OF
BIS(AMINOMETHYLBENZENE):
SYNTHESIS AND INFRARED STUDY**

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Abstract: The new adducts and complexes obtained have discrete or dimeric structures; in these structures the diamine behaves as a monodentate and hydrogen bonds involved or bidentate ligand. In one rare earth halide adduct the high coordination number (7) proposed is common for this family. When extra intermolecular hydrogen bonds are taken into account, supramolecular architectures may be obtained.

Keywords: *bidentate monodentate and hydrogen bonding involved
diamine, discrete structures, supramolecular architectures*

INTRODUCTION

The amines act widely as ligands in their neutral form or as adverse cations in their protonated forms [1]. Our group as some other research groups has been focusing since decades in developing the synthesis of new compounds containing oxoacid salts with amines for studying the behavior of the oxyanions as ligands [2 – 12]. In this paper we initiate the study of the interactions of a diamine-1,3C₆H₄(CH₂NH₂)₂ with di- and trihalides to follow its behavior as ligand. The obtained compounds have been characterized by elemental analyses and infrared spectroscopies then their structures were proposed on the basis of the obtained data.

MATERIALS AND METHODS

The studied adducts have been obtained as white powders allowing 1,3C₆H₄(CH₂NH₂)₂ to react with SnCl₂·2H₂O, HgCl₂, PrCl₃, ErCl₃·H₂O and ZnX₂ (X= Cl, Br) in defined ratio. The compounds **A**, **C**, **D**, **E**, **F** and **G** were obtained by mixing ethanolic solutions of C₆H₄(CH₂NH₂)₂ with SnCl₂·2H₂O, HgCl₂, PrCl₃, ErCl₃·H₂O, ZnBr₂ or ZnCl₂ in 1/1 ratio whereas the compound **B** was obtained as a white powder by allowing an ethanolic solution of C₆H₄(CH₂NH₂)₂ to react with an ethanolic solution of SnCl₂·2H₂O in 1/2 ratio. All 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 formulas:

A: 2C₆H₄(CH₂NH₂)₂·2H₂O·3SnCl₄; % C = 17.63 (17.34), % H = 2.59 (2.69), % N = 5.14 (5.07);

B: 3C₆H₄(CH₂NH₂)₂·2SnCl₄; % C = 31.01 (31.02), % H = 3.90 (3.63), % N = 9.04 (8.73);

C: 2C₆H₄(CH₂NH₂)₂·3HgCl₂·1/4C₆H₄(CH₂NH₂)₂·2H₂O; % C = 18.69 (19.13), % H = 2.70 (2.61), % N = 5.45 (5.41);

D: C₆H₄(CH₂NH₂)₂·ZnCl₂; % C = 35.26 (35.00), % H = 4.44 (4.50), % N = 10.28 (10.01);

E: C₆H₄(CH₂NH₂)₂·3ZnBr₂; % C = 11.84 (11.89), % H = 1.49 (1.50), % N = 3.45 (3.49);

F: 2C₆H₄(CH₂NH₂)₂·PrCl₃·3/2H₂O; % C = 35.15 (35.44), % H = 4.98 (5.02), % N = 10.25 (10.30);

G: C₆H₄(CH₂NH₂)₂·2ErCl₃·6H₂O; % C = 12.14 (11.71), % H = 3.06 (3.03), % N = 3.54 (3.46).

The elemental analyses were performed in “The Microanalyses Laboratory” from University of Burgundy-Dijon-France. The IR spectra were performed at the University of Burgundy-Dijon-France using a Bruker FTIR spectrometer. IR abbreviations: vs (very strong); s (strong); m (medium). The chemicals were purchased from Aldrich Company-Germany- without any further purification.

RESULTS AND DISCUSSION

Let us consider the main IR data in cm^{-1} of the tin (IV) adducts.

A: ν (NH) 3009 (s) 2906 (s), δ (NH) 1591 (s) 1473 (s) 1370 (s);

B: ν (NH) 2890 (s) 2681 (s) 2622 (s), δ (NH) 1596 (s) 1563 (m) 1513 (s) 1478 (s) 1374 (s).

It seems worthy to outline the oxidation of SnCl_2 into SnCl_4 in the two first adducts.

For **A** we suggest a discrete structure consisting of one internal SnCl_4 trans coordinated by the two amines and two external SnCl_4 being coordinated by one NH_2 group and one water molecule, the environment around the tin centres being octahedral (Figure 1).

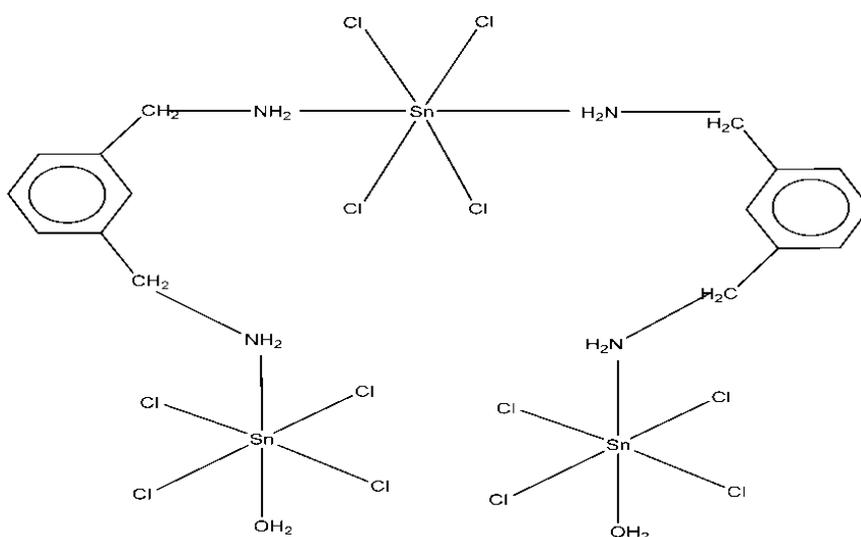


Figure 1. Proposed structure for **A**

The structure of **B** consists of a two metallic components one -with monodentate and hydrogen bonding involved amines- bridged by a bidentate amine, the environment around the tin atom being octahedral (Figure 2).

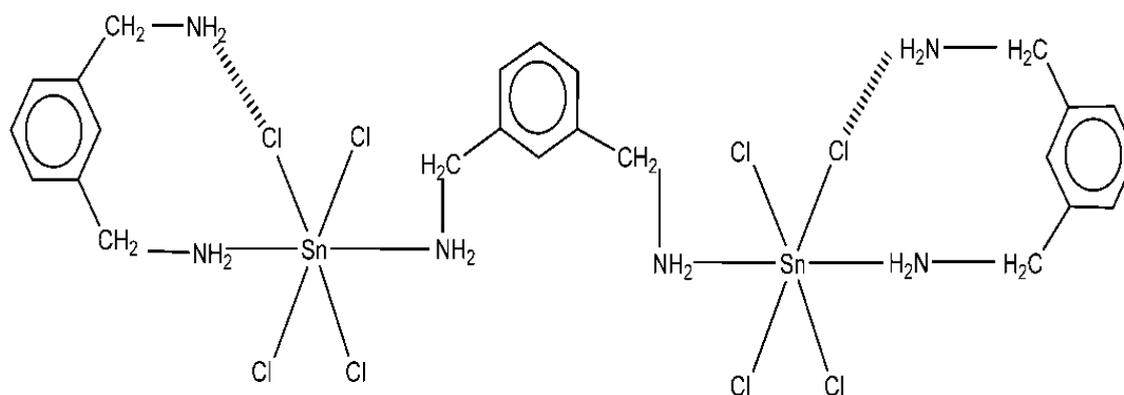


Figure 2. Proposed structure for **B**

Let us consider the main IR data of the three dihalides.

C: $\nu(\text{NH})$ 3248 (s) 3210 (s) 3129 (s), $\delta(\text{NH})$ 1563 (sh) 1494 (m) 1451 (s);

D: $\nu(\text{NH})$ 3284 (vs) 3237 (vs) 3130 (m) 3063 (m), $\delta(\text{NH})$ 1593 (vs) 1571 (vs) 1494 (vs) 1437 (s);

E: $\nu(\text{NH})$ 3548 (vs) 3435 (vs) 3282 (m) 3231 (m), $\delta(\text{NH})$ 1578 (m) 1490 (m) 1438 (m).

The suggested structure for **C** is discrete with two types of Hg metallic centers – one with a linear environment and two others in a tetrahedral one; the diamine behaves as a monocoordinating ligand involved in hydrogen bonding with chlorine atoms, these two centers being bridged by the third molecule of HgCl_2 (Figure 3).

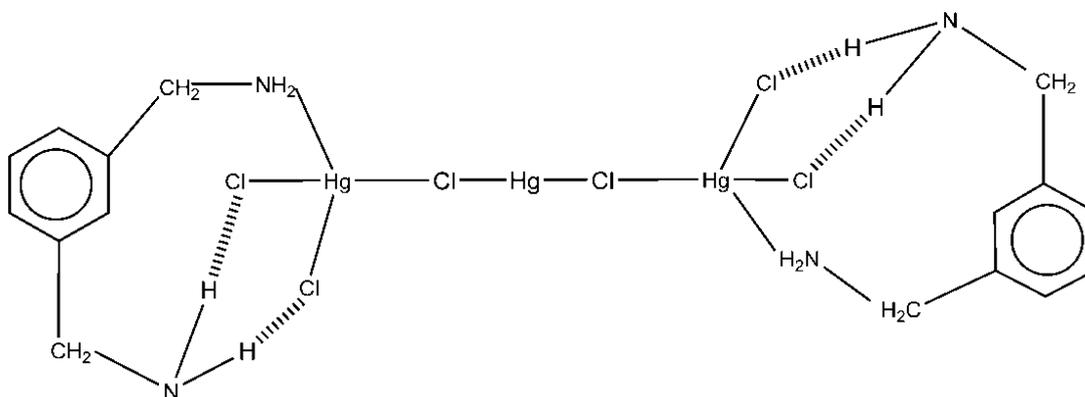


Figure 3. Proposed structure for **C**

For the zinc compounds we suggest:

- for the chlorine one a dimer with a bidentate amine coordinating two ZnCl_2 molecules leading to a tetrahedral environment around the zinc centers (Figure 4).

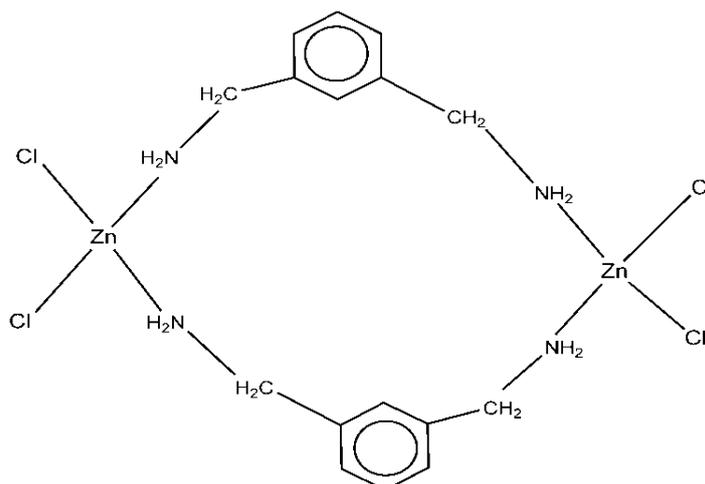


Figure 4. Proposed structure for **D**

- for the bromine one we suggest a discrete structure with a bidentate amine and Br bridges, the environment around the metallic centre being trigonal and tetrahedral (Figure 5).

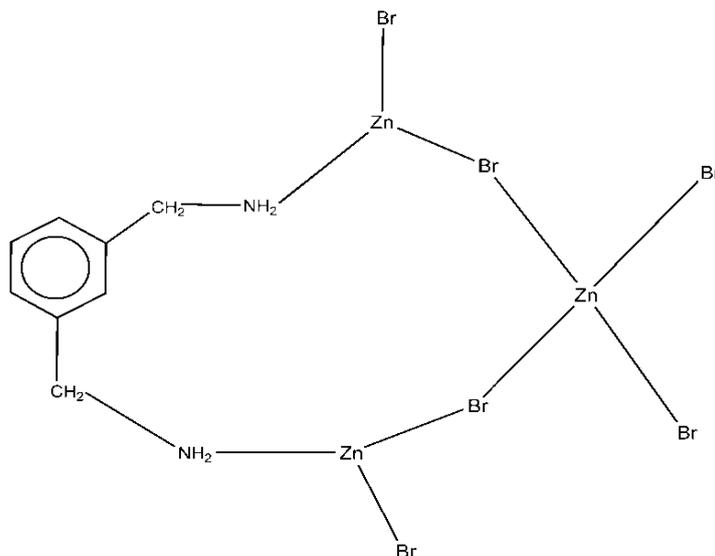


Figure 5. Proposed structure for **E**

Let us consider the main IR data of the rare earth metallic halides.

F: $\nu(\text{NH})$ 3306 (s) 3267(m)3184 (m), $\delta(\text{NH})$ 1627 (s) 1593 (s) 1515 (s) 1494 (s) 1442 (s);

G: $\nu(\text{NH})$ 3331 (s), $\delta(\text{NH})$ 1627 (m) 1497 (vs).

In the case of the PrCl_3 adduct we suggest a discrete structure in which the two amine molecules coordinate the Pr centre and are involved in hydrogen bonds with chlorine atoms, the water molecule being a coordinating one (Figure 6).

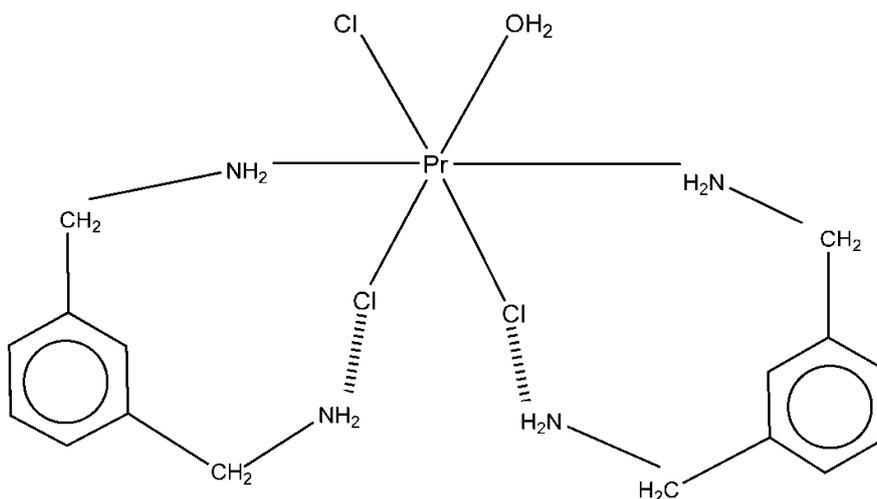


Figure 6. Proposed structure for **F**

In the case of ErCl_3 adduct the amine is a bidentate ligand coordinating the Er centers, the six water molecules are also coordinating ones – three water molecules coordinate each Er centre. The structure is discrete, the coordinating number around Er is 7 (Figure 7).

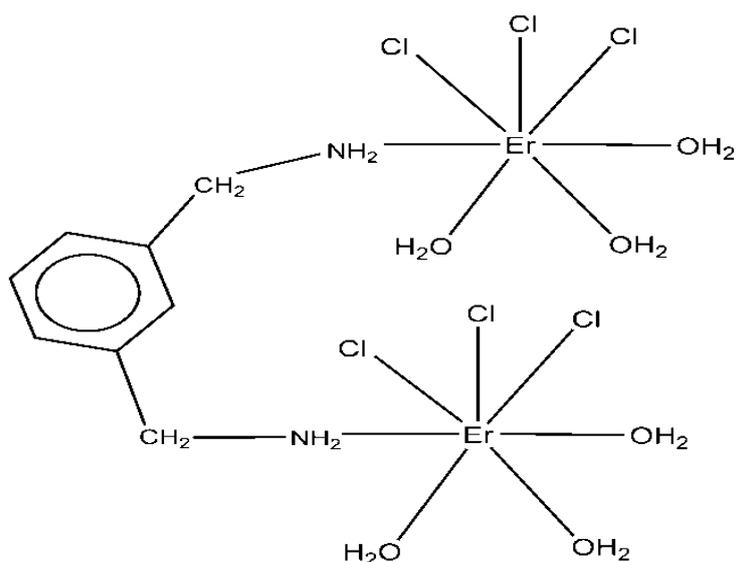


Figure 7. Proposed structure for **G**

This high coordination number is very common in rare earth elements chemistry [1]. In all the suggested structures when extra hydrogen bonds are considered, supramolecular architectures may be obtained.

CONCLUSION

The amine behaves a bidentate or a monodentate and hydrogen bonding involved ligand. The oxidation of SnCl₂ into SnCl₄ in the tin compounds is noteworthy. The suggested structures are discrete-monomeric or dimeric-. The high coordination number for one rare earth metallic halide adduct is common for these metallic centers. Supramolecular architectures may be obtained when extra inter molecular hydrogen bonds are considered.

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