

Communication

Hybrid Pyridine *Bis*-Anthracene-Imidazolium Salt: NMR Studies on Zn-Acetate Complexation

Dorina Amăriucăi-Mantu ¹, Violeta Mangalagiu ², Catalina-Ionica Ciobanu ² and Vasilichia Antoci ^{1,*}

¹ Faculty of Chemistry, Alexandru Ioan Cuza University of Iasi, 11 Carol 1st Blvd, 700506 Iasi, Romania; dorina.mantu@uaic.ro

² Institute of Interdisciplinary Research-CERNESIM Center, Alexandru Ioan Cuza University of Iasi, 11 Carol I, 700506 Iasi, Romania; violeta.mangalagiu@uaic.ro (V.M.); catalina.ciobanu@uaic.ro (C.-I.C.)

* Correspondence: vasilichia.antoci@uaic.ro; Tel.: +40-232-2011022535

Abstract: We report here the design and synthesis of a new hybrid *bis*-anthracene-imidazolium salt, having a pyridine scaffold. NMR studies of dimer generation, as well as complexation with zinc acetate were performed.

Keywords: hybrid salt; dimer generation; Zn complexation; NMR studies



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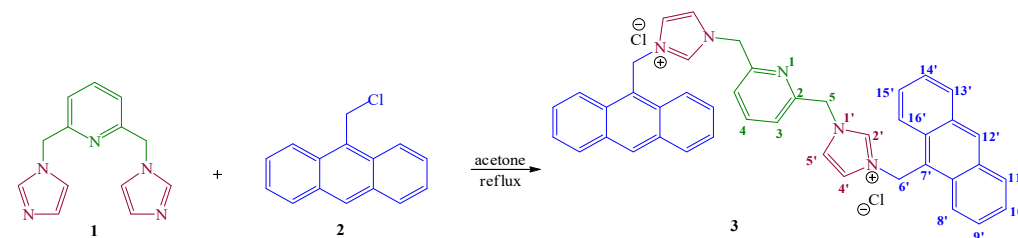
1. Introduction

In the field of supramolecular chemistry, the design and synthesis of chemosensors for the detection of metal ions have been widely exploited, due to their biological and environmental significance [1–3]. Most of these receptors can be considered hybrid compounds based on a moiety of imidazole, benzimidazole and pyridine, attached to the fluorophore, which is the anthracene unit [1–5].

Considering our experience in the field of the synthesis of hybrid compounds with imidazole/benzimidazole, pyridine and anthracene units [2,6–11], and our previous experience in the area of cycloimmonium ylides [12–22], we decided to synthesize a novel hybrid pyridine *bis*-anthracene-imidazolium salt, and also to study its complexation to Zn acetate by NMR.

2. Results and Discussion

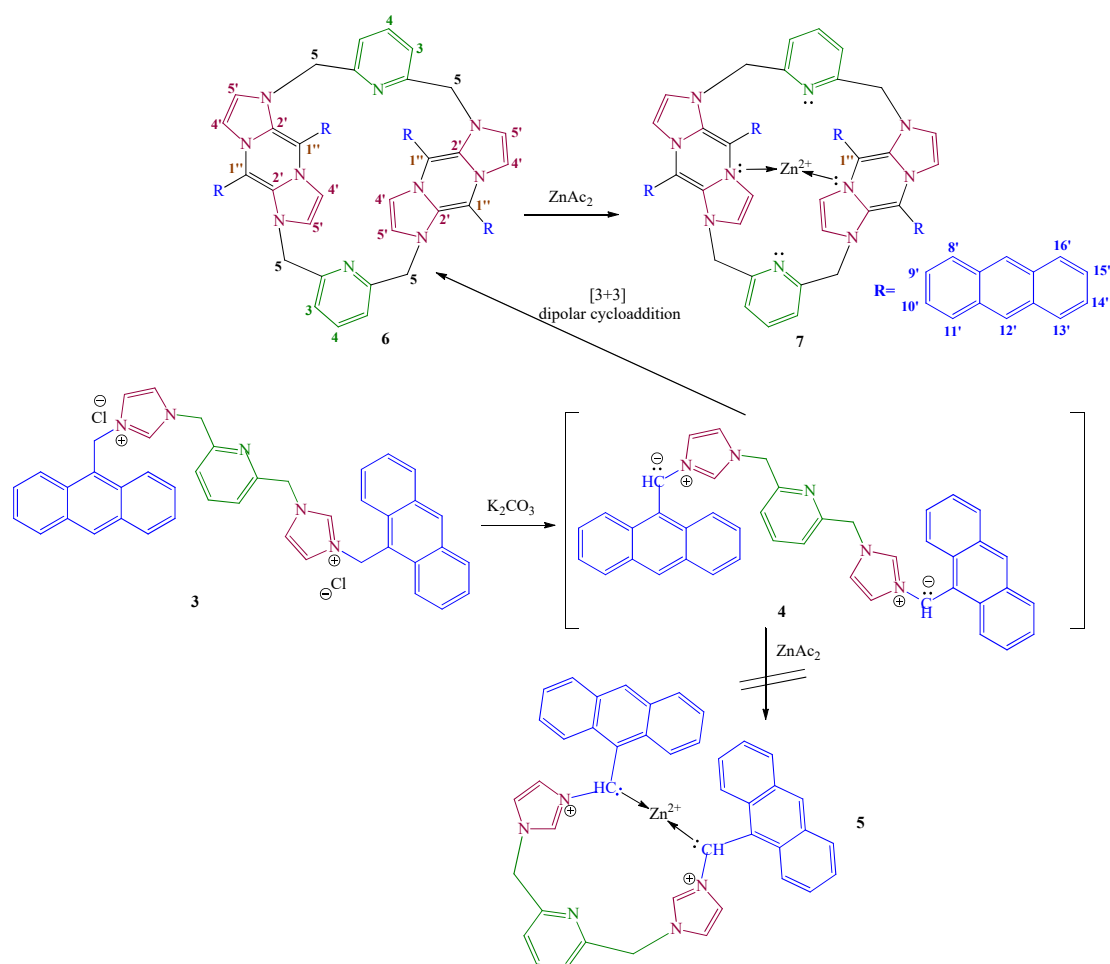
The reaction pathway to obtain the new hybrid pyridine *bis*-anthracene-imidazolium salt **3** involve a quaternization reaction of 2,6-*bis*-(1*H*-imidazol-1-yl)methylpyridine **1**, previously reported [7], with 9-(chloromethyl)anthracene **2**, Scheme 1. The structure of new hybrid salt **3** was proved by NMR experiments (¹H-, ¹³C- NMR, 2D: COSY, HMQC, HMBC).



Scheme 1. The route of synthesis of hybrid pyridine *bis*-anthracene-imidazolium salt **3**.

In the next stage, we studied the complexation process of ylide **4** with Zn²⁺ cation [Zn²⁺ cation was generated from aqueous deuterated solution of zinc acetate (1.25 × 10^{−2} M)]. The ylide **4**, was generated in situ from the corresponding *bis*-anthracene-imidazolium salt **3** [previous dissolved in deuterated DMSO (2.5 × 10^{−3} M)] using aqueous deuterated solutions of potassium carbonate (2 × 10^{−3} M and 2.5 × 10^{−1} M).

Our expectation was to obtain a complex of ylide **4** with Zn^{2+} of type **5**, Scheme 2 as in related cases [5]. Instead, because of high reactivity of ylide **4**, a dimerisation process took place (*via* a 3 + 3 dipolar cycloaddition of an ylide molecule to another) when the dimeric structure type **6** was obtained. In the next step, the dimer **6** complexes with Zn^{2+} , leading to the final product, the dimer complex with Zn^{2+} , type **7**. The structure of Zn complex, type **7**, is a proposed structure but different coordination of Zn^{2+} ion cannot be excluded.



Scheme 2. The complexation process with Zn^{2+} of ylide **4**.

In Figure 1 are presented the overlapped ^1H -NMR spectra of salt **3**, dimeric structure **6** and dimeric complex with Zn^{2+} type **7**. Here are described the quantities of reactants used in the experiments and the exchange of the color of solutions.

In the ^1H -NMR spectrum of dimeric structure type **6** it can be observed the disappearance of protons $(-\text{CH}_2-)_{6'}$, which in salt **3** appears as a singlet at 6.48 ppm. Also, the signal around 9.06 ppm of $\text{H}_{2'}$ from imidazole nucleus of salt **3** does not appear in the NMR spectrum of dimer **6**.

The dimer complexation with Zn^{2+} induces a visible shielding effect on the chemical shifts of the protons from aliphatic and aromatic zone.

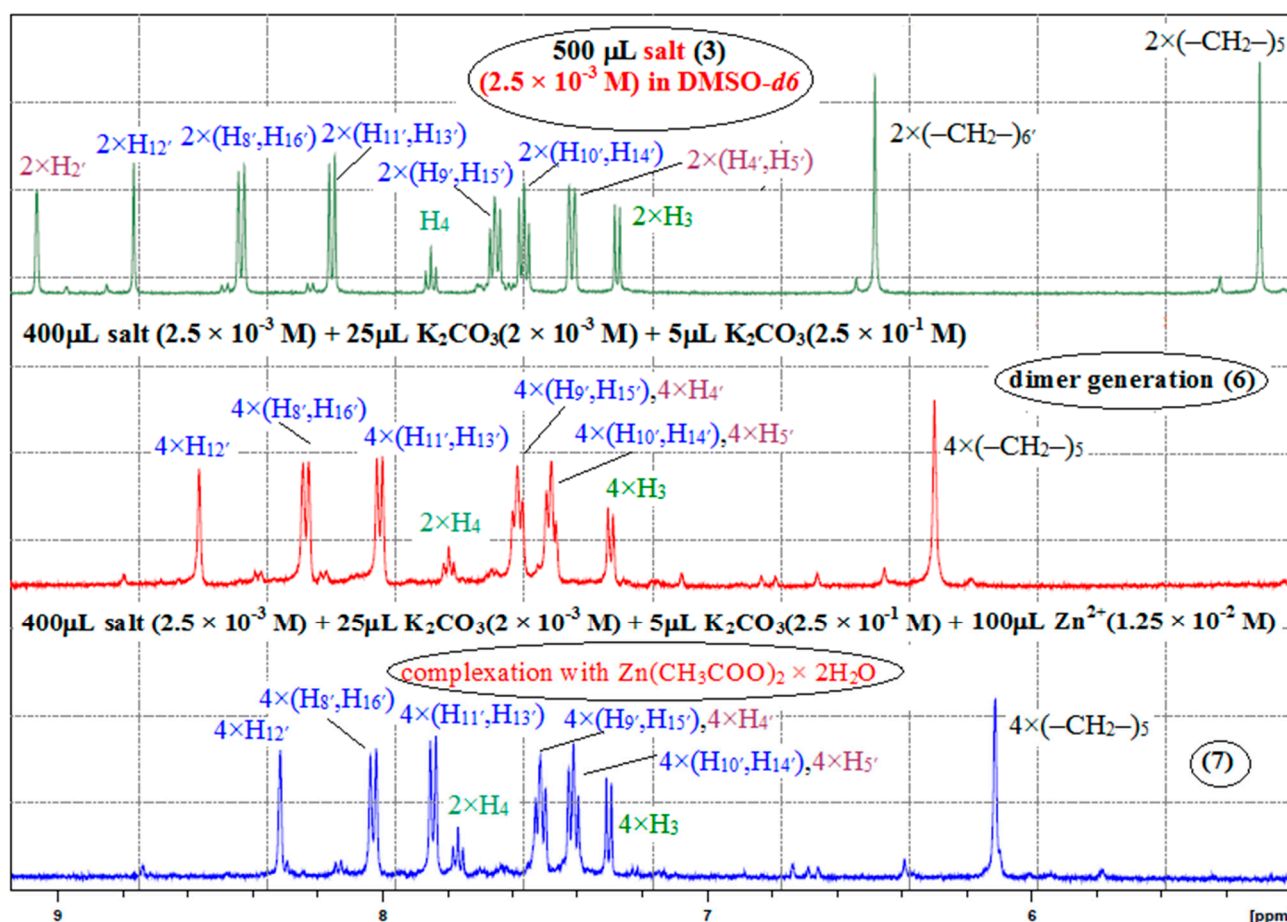


Figure 1. The ^1H -NMR spectra of salt 3, dimeric structure 6 and dimeric complex 7.

3. Materials and Methods

3.1. Instrumentation

The solvents and reagents were purchased from commercial sources, being used without further purification. The melting point (uncorrected) of compound 3 was determined using an open capillary tubes introduced in a MEL-TEMP Electrothermal apparatus. The nuclear magnetic resonance experiments have been recorded on a Bruker AVANCE III 500 MHz spectrometer (Iasi, Romania), equipped with a 5 mm PABBO detection probe, operating at 500.19 and 125.7 MHz for ^1H and respectively ^{13}C nuclei. In ^1H and ^{13}C spectra, chemical shifts are reported in δ units (ppm) relative to the residual peak of solvent (ref: $\text{DMSO-}d_6$, ^1H : 2.50 ppm; ^{13}C : 39.52 ppm). The coupling constants (J) are given in Hz. In the NMR spectra to appointed the multiplicity of signals, were used the abbreviations: s = singlet, d = doublet, t = triplet. The microanalyses were in satisfactory agreement with the calculated values: C, ± 0.15 ; H, ± 0.10 ; N, ± 0.30 .

3.2. General Procedure for Synthesis of Hybrid Quaternary Salt 3

To a solution of 2,6-bis((1H-imidazol-1-yl)methyl)pyridine 1 (1 mmol, 1 equiv., 0.24 g, dissolved in 40 mL acetone using the ultrasound bath) was added dropwise a solution of 9-(chloromethyl)anthracene 2 (2.8 mmol, 2.8 equiv., 0.63 g, dissolved in 15 mL acetone using the ultrasound bath). The reaction mixture was refluxed for 12 h, and stirred at room temperature for another 24 h to give the corresponding hybrid quaternary salt 3. The completion of the reaction was carried out using TLC. The obtained salt was filtered off, washed two times with the same solvent (10 mL) and dried *in vacuum*. No other purification required.

1,1'-(pyridine-2,6-diylbis(methylene))bis(3-(anthracen-9-ylmethyl)-1H-imidazol-3-ium) chloride (3): Light brown powder. mp 223–224 °C. $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$) (ppm): 9.06 (s, 2H, $2\times\text{H}_{2'}$), 8.76 (s, 2H, $2\times\text{H}_{12'}$), 8.43 (d, 4H, $J = 9.0$ Hz, $2\times(\text{H}_{8'},\text{H}_{16'})$), 8.15 (d, 4H, $J = 8.5$ Hz, $2\times(\text{H}_{11'},\text{H}_{13'})$), 8.85 (t, 1H, $J = 8.0$ Hz, H_4), 7.75 (t, 4H, $J = 8.5$ Hz, $J = 7.0$ Hz, $2\times(\text{H}_{9'},\text{H}_{15'})$), 7.56 (t, 4H, $J = 8.0$ Hz, $J = 7.0$ Hz, $2\times(\text{H}_{10'},\text{H}_{14'})$), 7.41 (d, 4H, $J = 9.0$ Hz, $2\times(\text{H}_{4'},\text{H}_{5'})$), 7.27 (d, 2H, $J = 8.0$ Hz, $2\times\text{H}_3$), 6.48 (s, 4H, $2\times(-\text{CH}_2-)_{6'}$), 5.29 (s, 4H, $2\times(-\text{CH}_2-)_{5'}$). $^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO-}d_6$) (ppm): 153.5 ($2\times\text{C}_2$), 138.8 (C_4), 136.5 ($2\times\text{C}_{2'}$), 131.0 ($2\times(\text{C}_{11'a},\text{C}_{12'a})$), 130.6 ($2\times(\text{C}_{7'a},\text{C}_{16'a})$), 130.1 ($2\times\text{C}_{12'}$), 129.3 ($2\times(\text{C}_{11'},\text{C}_{13'})$), 127.7 ($2\times(\text{C}_{9'},\text{C}_{15'})$), 125.5 ($2\times(\text{C}_{10'},\text{C}_{14'})$), 123.6 ($2\times\text{C}_{7'}$), 123.5 ($2\times(\text{C}_{8'},\text{C}_{16'})$), 123.1 ($2\times\text{C}_{4'}$), 122.1 ($2\times\text{C}_{5'}$), 122.0 ($2\times\text{C}_3$), 52.5 ($2\times(-\text{CH}_2-)_{5'}$), 44.9 ($2\times(-\text{CH}_2-)_{6'}$). Anal. Calcd. for $\text{C}_{43}\text{H}_{35}\text{Cl}_2\text{N}_5$ C, 74.56; H, 5.09; N, 10.11. Found C, 74.66; H, 5.19; N, 10.01.

3.3. General Procedure for NMR Studies

3.3.1. Dimer Generation 6

To 400 μL (2.5×10^{-3} M) solution in $\text{DMSO-}d_6$ of hybrid quaternary salt 3 was added 25 μL (2×10^{-3} M) solution in D_2O of K_2CO_3 and also 5 μL (2.5×10^{-1} M) solution of K_2CO_3 . It was observed that the solution become pale pink when adding the base (K_2CO_3). After the preparation of the solution, the NMR spectra were registered and the existence of the dimer 6 was highlighted.

Weak pink solution. $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$) (ppm): 8.56 (s, 4H, $4\times\text{H}_{12'}$), 8.23 (d, 8H, $J = 8.5$ Hz, $4\times(\text{H}_{8'},\text{H}_{16'})$), 8.00 (d, 8H, $J = 8.0$ Hz, $4\times(\text{H}_{11'},\text{H}_{13'})$), 7.79 (t, 2H, $J = 8.0$ Hz, $2\times\text{H}_4$), 7.58 (t, 12H, $J = 7.0$ Hz, $J = 7.5$ Hz, $4\times(\text{H}_{9'},\text{H}_{15'},\text{H}_{4'})$), 7.48 (t, 12H, $J = 7.0$ Hz, $J = 8.0$ Hz, $4\times(\text{H}_{10'},\text{H}_{14'},\text{H}_{5'})$), 7.29 (d, 4H, $J = 7.5$ Hz, $4\times\text{H}_3$), 6.30 (s, 8H, $4\times(-\text{CH}_2-)_{5'}$). $^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO-}d_6$) (ppm): 157.7 ($4\times\text{C}_{2'}$), 153.5 ($4\times\text{C}_2$), 139.2 ($2\times\text{C}_4$), 131.2 ($4\times(\text{C}_{11'a},\text{C}_{12'a})$), 130.8 ($4\times(\text{C}_{7'a},\text{C}_{16'a})$), 130.5 ($4\times\text{C}_{12'}$), 129.7 ($4\times(\text{C}_{11'},\text{C}_{13'})$), 128.2 ($4\times(\text{C}_{4'},\text{C}_{9'},\text{C}_{15'})$), 127.5 ($4\times\text{C}_{1'}$), 125.9 ($4\times(\text{C}_{5'},\text{C}_{10'},\text{C}_{14'})$), 123.4 ($4\times(\text{C}_{7'},\text{C}_{8'},\text{C}_{16'})$), 122.3 ($4\times\text{C}_3$), 45.9 ($4\times(-\text{CH}_2-)_{5'}$).

3.3.2. Dimer Complex with Zn^{2+} 7

To the solution of generated dimer 6 (400 μL (2.5×10^{-3} M) salt 3, 25 μL (2×10^{-3} M) K_2CO_3 , 5 μL (2.5×10^{-1} M) K_2CO_3) was added 100 μL (1.25×10^{-2} M) solution in D_2O of $\text{Zn}(\text{CH}_3\text{COO})_2 \times 2\text{H}_2\text{O}$, when the solution becomes poorly colored. After the preparation of the solution, the NMR spectra were recorded and the complex formation with zinc ions was evidenced.

Poorly colored solution. $^1\text{H-NMR}$ (500 MHz, $\text{DMSO-}d_6$) (ppm): 8.31 (s, 4H, $4\times\text{H}_{12'}$), 8.02 (d, 8H, $J = 8.5$ Hz, $4\times(\text{H}_{8'},\text{H}_{16'})$), 7.84 (d, 8H, $J = 8.5$ Hz, $4\times(\text{H}_{11'},\text{H}_{13'})$), 7.76 (t, 2H, $J = 8.0$ Hz, $2\times\text{H}_4$), 7.51 (t, 12H, $J = 7.0$ Hz, $J = 8.5$ Hz, $4\times(\text{H}_{9'},\text{H}_{15'},\text{H}_{4'})$), 7.41 (t, 12H, $J = 7.5$ Hz, $4\times(\text{H}_{10'},\text{H}_{14'},\text{H}_{5'})$), 7.30 (d, 4H, $J = 8.0$ Hz, $4\times\text{H}_3$), 6.11 (s, 8H, $4\times(-\text{CH}_2-)_{5'}$). $^{13}\text{C-NMR}$ (125 MHz, $\text{DMSO-}d_6$) (ppm): 177.5 ($4\times\text{C}_{2'}$), 153.6 ($4\times\text{C}_2$), 139.9 ($2\times\text{C}_4$), 131.6 ($4\times(\text{C}_{11'a},\text{C}_{12'a})$), 131.3 ($4\times\text{C}_{1'}$), 131.2 ($4\times\text{C}_{12'}$), 130.3 ($4\times(\text{C}_{11'},\text{C}_{13'})$), 129.0 ($4\times(\text{C}_{4'},\text{C}_{9'},\text{C}_{15'})$), 126.5 ($4\times(\text{C}_{5'},\text{C}_{10'},\text{C}_{14'})$), 123.6 ($4\times(\text{C}_{8'},\text{C}_{16'})$), 123.3 ($4\times\text{C}_{7'}$), 123.1 ($4\times\text{C}_3$), 45.6 ($4\times(-\text{CH}_2-)_{5'}$).

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