

Some Maleate New Tin (IV) and Magnesium or Zinc Chloride Adduct and Derivative: Synthesis and Spectroscopic Study

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Abstract: Three new maleate compounds have been synthesized and studied by infrared, ^{25}Mg NMR (Nuclear Magnetic Resonance) Spectroscopy and UV (Ultraviolet)-visible spectroscopies. The suggested structures for the three complexes are discrete with NH-Cl hydrogen bonds. The maleate anion is monochelating (compound 1 and 2) and bichelating (compound 3). The environment tin (IV) and magnesium center are octahedral and the zinc center environment is tetrahedral. In all the suggested structures, when extra hydrogen bonds are considered, supramolecular architectures are obtained.

Key words: Discrete structures, hydrogen bonds, monochelating, bichelating, octahedral or tetrahedral environments, maleate, supramolecular.

1. Introduction

Maleic acid is a key molecule in crystal engineering due to its structural aspect in deprotonation and inter and intramolecular hydrogen bonding functionality. It is recognized as an effective ingredient in pharmaceutical formulations and has been placed on a list of pharmaceutically and medically acceptable acids [1, 2]. Maleate anions are frequently used to prepare complexes, organic compounds, and especially pharmaceutical and medically products [3-7]. As a dicarboxylic acid, it forms two salts with active pharmaceutical ingredients: MAL (Maleates) and HMAL (Hydrogen-Maleates). In pharmacokinetics, for example, some maleate salts are used as the free basis or enalapril maleate to study the influence of some active agents in healthy patients [8, 9]. In genetic medicine, maleate salts are used as amlodipine salts in genetic disease treatment [10]. In fundamental chemistry, Madsen et al. [11] reported the alkylammonium hydrogen maleate and studied the very

short intermolecular hydrogen bonds. Poręba et al. [12] have reported structures of alkali maleates. Thus, to better understand the mode of formation of maleates, three new complexes $(\text{EtNH}_3)_2[\text{C}_4\text{H}_2\text{O}_4(\text{SnCl}_4)]$ (1), $(\text{EtNH}_3)_2[\text{C}_4\text{H}_2\text{O}_4\text{MgCl}_2(\text{H}_2\text{O})_2]$ (2) and $(\text{MeNH}_3)_2[\text{C}_4\text{H}_2\text{O}_4(\text{ZnCl}_2)_2]\cdot 2\text{H}_2\text{O}$ (3) were isolated by doing react to the maleic acid, the alkylammonium and SnCl_4 or $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ or ZnCl_2 in one “pot” process.

2. Materials and Methods

Adding a mixture maleic acid ($n = 3$ mmol), EtNH_2 ($n = 3$ mmol) and SnCl_4 ($n = 3$ mmol) in 30 mL of methanol solvent, a white precipitate is obtained after 2 h of stirring at room temperature. This precipitate is filtered and the filtrate is evaporated slowly and the suitable crystal is obtained. A mixture of maleic acid ($n = 3$ mmol), EtNH_2 ($n = 6$ mmol) and $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ ($n =$ mmol), in 30 mL of absolute methanol solvent, gives a limpid solution after 2 h reflux at 80°C . This solution is submitted to slow solvent evaporation. After one

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Table 1 Suggested formulae of synthesized compounds and the elemental analyses.

Compound	Chemical formulae	Elemental analyses (%)					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
1	(EtNH ₃) ₂ [C ₄ H ₂ O ₄ (SnCl ₄)]	20.58	20.30	8.88	8.89	6.00	6.02
2	(EtNH ₃) ₂ [C ₄ H ₂ O ₄ MgCl ₂ (H ₂ O) ₂]	26.00	25.93	6.00	6.11	7.56	7.44
3	(MeNH ₃) ₂ [C ₄ H ₂ O ₄ (ZnCl ₂) ₂].2H ₂ O	20.56	20.22	5.17	5.30	7.98	7.90

week, a suitable crystal is obtained. When maleic acid ($n = 3$ mmol) is reacted with MeNH₂ ($n = 6$ mmol) and ZnCl₂ ($n = 3$ mmol) in 30 mL of ethanol + water solvent, a clear solution is obtained after 2 h steered up. The analytical data are given in Table 1.

The elemental analyses have been obtained from the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France. The ²⁵Mg NMR (Nuclear Magnetic Resonance) spectra were performed at the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France using a Bruker Avance 400 MHz Spectrometer with a low sensitivity band. The IR (Infrared) spectra of the compounds were recorded at room temperature using an FTIR (Fourier Transform Infrared) spectrometer at the University Cheikh Anta Diop Dakar and at the Institute of Molecular Chemistry of the University of Burgundy, Dijon-France (over a range from 4,500 to 400 cm⁻¹) in the form of suspension of powders in Nujol or crushed dry. The UV-visible have been obtained from the spectrometer at the University Cheikh Anta Diop Dakar.

3. Results and Discussion

Let us consider the IR, ¹¹⁹Sn NMR and UV-visible data.

IR(cm⁻¹): 1: ν (NH) = 2,935 (br); ν as (COO⁻) = 1,591 (br); 1,505 (s); ν s (COO⁻) = 1,377 (s); 1,324 (s); δ (COO⁻) = 895 (vs), 786 (vs); ν (Sn-O) = 589 (m)

2: ν (NH) = 2,936 (br); ν (OH) = 3,100 (br); δ (NH) = 1,445 (s); δ (OH) = 1,350 (s), ν as (COO⁻) = 1,617 (s); 1,493 (vs); ν s (COO⁻) = 1,377 (s), 1,324 (vs); δ (COO⁻) = 895 (s); 846 (s); ν (Mg-O) = 601 (m); 3: ν (NH) = 2,926 (br); ν (OH) = 3,425 (br); δ (NH) = 1,404 (s); ν as

(COO⁻) = 1,680 (vs); 1,479 (m); ν s (COO⁻) = 1,440 (s); 1,350 (s); δ (COO⁻) = 895 (s); 840 (s); ν (Zn-O) = 590 (w); ²⁵Mg NMR (CDCl₃, ppm): 2: δ = 0.14(s), UV visible (nm): 1: λ _{max} = 294(vs); 2: λ _{max} = 291(vs); 3: λ _{max} = 292(s); 345 (vs).

From these spectroscopic data, we have suggested the following compounds.

3.1 (EtNH₃)₂[C₄H₂O₄(SnCl₄)] (1)

The infrared spectrum of the compound shows a broad band centered at 2,935 cm⁻¹ due to the presence of the EtNH₃⁺ cation. This band likely indicates the existence of hydrogen bonds. Several bands appear in the valence region of the maleate anion, with a broad band at 1,591 cm⁻¹ corresponding to the antisymmetric stretching vibration of the carboxylate anion. At a lower frequency, around 589 cm⁻¹; the medium band is attributed to the Sn-O vibration [13], confirming the complexation of tin. The strong band observed at 294 nm in the UV-visible spectrum of the compound can be attributed solely to the various $\pi \rightarrow \pi^*$ transitions associated with the ethylene double bond (CH₂=CH₂) of the maleate anion and the carbonyl groups (C=O) [14]. These UV-visible results are consistent with the infrared data. Based on the spectroscopic data, the proposed structure for compound 1 is discrete (Fig. 1). The maleate anion is a monochelating ligand, and the environment around the tin is octahedral. The equatorial positions are occupied by two oxygen atoms from the anion and two chlorine atoms. The other two chlorine atoms occupy the axial positions. The cation participates through NH...Cl hydrogen bonds, ensuring the stability of the compound.

Some Maleate New Tin (IV) and Magnesium or Zinc Chloride Adduct and Derivative:
Synthesis and Spectroscopic Study

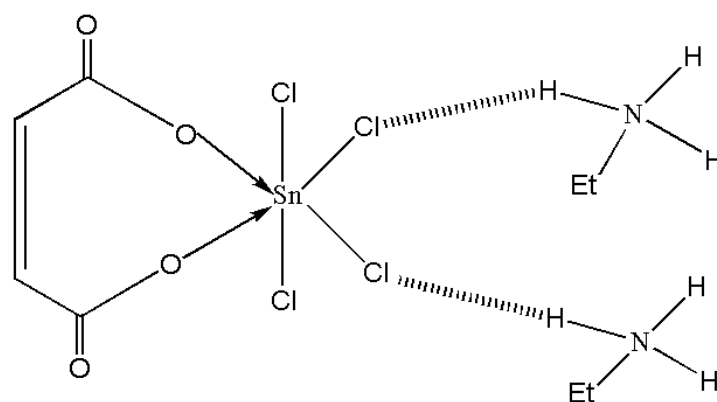


Fig. 1 Proposed structure for the compound 1.

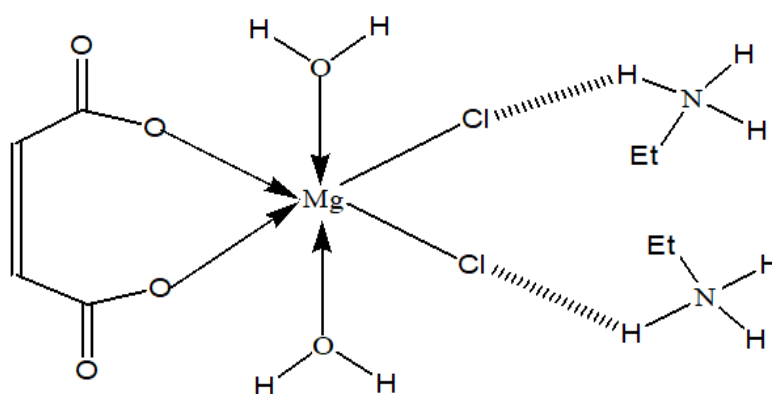


Fig. 2 Proposed structure for the compound 2.

3.2 $(EtNH_3)_2[C_4H_2O_4MgCl_2(H_2O)_2]$ (2)

While considering the IR of the compound 2, several bands appear in the valence region of the maleate anion. The strong band at $1,493\text{ cm}^{-1}$ confirms the presence of the maleate anion. The broad band centered at $2,936\text{ cm}^{-1}$ is attributed to the presence of hydrogen bonds, while the band at $3,100\text{ cm}^{-1}$ indicates the presence of water molecules. Additionally, the medium band observed at 610 cm^{-1} [15] is due to the Mg-O vibration, showing the coordination between magnesium and the maleate ligand through these oxygen atoms. The NMR spectrum of magnesium shows a unique signal at 0.14 ppm, distinct from the reference signal ($\delta(\text{MgCl}_2) = 0.00\text{ ppm}$) [16]. This chemical shift value indicates significant perturbation of the environment around the magnesium, confirming the complexation of magnesium center. The strong band that appears at 291 nm in the UV-visible spectrum of the compound can be attributed

solely to the various $\pi \rightarrow \pi^*$ transitions associated with the ethylene double bond ($\text{CH}_2=\text{CH}_2$) of the maleate anion and the carbonyl groups ($\text{C}=\text{O}$) [14]. These UV-visible results are consistent with the infrared data. From the spectroscopic data, the proposed structure in the compound 2 is discrete, with the anion being a monochelating ligand and the environment around the octahedral magnesium. The cation is involved through N-H...Cl hydrogen bonds.

3.3 $(MeNH_3)_2[C_4H_2O_4(ZnCl_2)_2] \cdot 2H_2O$ (3)

The IR spectrum of the compound shows several absorption bands in the valence region of the carboxylate anion, and the strong band at $1,680\text{ cm}^{-1}$ strongly confirms the presence of the carboxylate anion. The two broad bands centered at $2,926$ and $3,425\text{ cm}^{-1}$ are attributed to the presence of the cation MeNH_3^+ and water molecules, respectively. The weak band observed at the lower frequency of 590 cm^{-1} is due to the Zn-O bond [17].

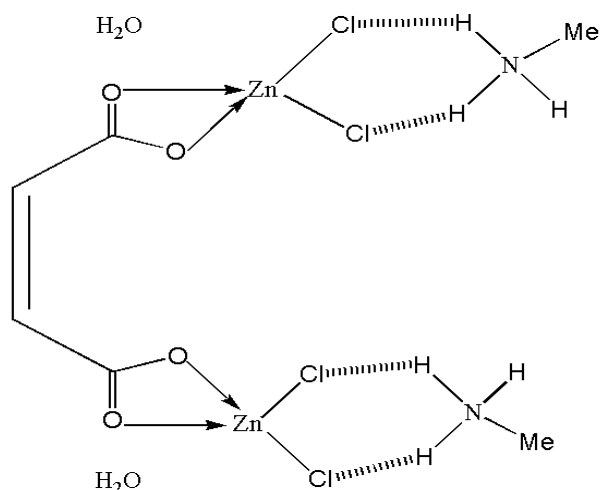


Fig. 3 Proposed structure for the compound 3.

In the UV-visible spectrum, the strong band observed at 291 nm can be attributed solely to the different $\pi \rightarrow \pi^*$ transitions associated with the ethylene double bond ($\text{CH}_2=\text{CH}_2$) of the maleate anion and the carbonyl groups ($\text{C}=\text{O}$). The very strong band at 345 nm [14] is attributed to $n \rightarrow \pi^*$ transitions based on the lone pairs of electrons on the oxygen atoms of the maleate. Through these spectroscopic data, the proposed structure is a discrete structure (Fig. 3). The maleate anion acts as a bidentate ligand through its carboxylate function, and the environment around the metal center is tetrahedral. The cation is involved in the structure through N-H...Cl hydrogen bonding, while water molecules serve as network molecules.

4. Conclusion

The studied adducts and complex have a discrete structure, the maleate anions behaving as a bichelating or monochelating ligand. The environments around the tin or magnesium center are octahedral and the environment around the zinc being tetrahedral. In the structures containing free OH or NH groups extra intermolecular hydrogen bonds can be considered leading to supramolecular architectures.

List of Notations

IR abbreviations: Br (Broad), (VS) Very Strong, (S) Strong, (M) Medium, (W) Weak.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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**Some Maleate New Tin (IV) and Magnesium or Zinc Chloride Adduct and Derivative:
Synthesis and Spectroscopic Study**

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