

NEW ZINC OXALATO AND HYDROGENOXALATO COMPLEXES: SYNTHESIS AND INFRARED STUDY

GORGUI AWA SECK¹, LIBASSE DIOP^{1*}, ABOUBACRY SENE¹

¹University Cheikh Anta Diop, Faculty of Sciences and Technics, Department of Chemistry, Laboratory of Mineral and Analytical Chemistry, DAKAR, Senegal

Abstract: Five new oxalato and hydrogenoxalato complexes with ZnBr₂ have been synthesized and studied by infrared. Discrete structures have been suggested in the basis of spectroscopic data. The environments around the zinc centre being trigonal bipyramidal, tetrahedral, octahedral or monocapped octahedral. The anions behave as monochelating ligands. When the cations and OH group are involved in extra hydrogen bonds, a supramolecular architecture may be obtained.

Keywords: discrete structures, hydrogen bonds, IR technic, monochelating oxoanions, monocapped octahedral, oxalato and hydrogenoxalato complexes

1. INTRODUCTION

Hathaway [1] has summarized the data on the coordination ability of oxyanions; our group and many other research groups worldwide have published several papers on this topic [2-8]. In this dynamic we initiate here the study of the interactions between (Et₃NH)HC₂O₄ or (Et₃NH)₂C₂O₄ and ZnBr₂ which has yielded five new complexes, infrared study of which have been carried out then structures suggested on the basis of spectroscopic data.

2. EXPERIMENTAL SETUP

(Et₃NH)HC₂O₄ (L₁) -[%Calculated (% Found): % C = 50.25(50.19), % H = 8.96(8.67), % N = 7.32(7.42)]- and (Et₃NH)₂C₂O₄ (L₂) -[% C = 57.50(57.10), % H = 11.03(10.87), % N = 9.58(9.53), have been obtained as crystals on semi-or totally neutralizing oxalic acid with Et₃N in water and allowing the obtained solution to evaporate in the oven at 60 °C.

When (L₁) is allowed to react with ZnBr₂ in ethanol in the ratio 2/1 for **A**, 1/1 for **B**, and 1/2 for **C**, white powders are collected after a slow solvent evaporation. When ethanolic solutions of (L₂) are allowed to react with ZnBr₂ in 1/1 ratio for **D** and 2/1 for **E**, white precipitates are obtained, stirred around two hours and filtered. The analytical data [% Calculated (% Found)], (Table 1), have allowed suggesting the following formulae:

A: (Et₃NH)HC₂O₄.Zn(HC₂O₄)₂.1/4Et₃NHBr

B: (Et₃NH) HC₂O₄.ZnBr₃HNEt₃.2H₂O

C: (Et₃NH)HC₂O₄.Et₃NHBr.Zn(HC₂O₄)₂.1/8Et₃NHBr

* Corresponding author, email: dlibasse@gmail.com

D: $(\text{Et}_3\text{NH})_2\text{C}_2\text{O}_4 \cdot \text{ZnC}_2\text{O}_4 \cdot \text{ZnBr}_2 \cdot \text{Et}_3\text{NHBr} \cdot \text{EtOH}$

E: $(\text{Et}_3\text{NH})_2\text{C}_2\text{O}_4 \cdot \text{ZnC}_2\text{O}_4 \cdot \text{ZnBr}_2 \cdot \text{Et}_3\text{NHBr}$

Table 1. Analytical data.

Complex	% C	% H	% N
A	33.89(33.70)	4.81(4.60)	3.66(3.58)
B	26.50(26.70)	5.88(5.65)	4.41(4.28)
C	35.34(35.32)	5.81(5.79)	4.67(4.65)
D	32.06(32.05)	6.05(6.03)	4.67(4.65)
E	30.97(30.95)	5.67(5.64)	4.93(4.92)

The elemental analyses have been obtained from the Microanalyses Laboratory (University of Burgundy, Dijon-France). The infrared spectra have been obtained from the University of Caen-France using a Bruker FT-IR spectrometer. IR abbreviations: broad (br), very strong (vs), strong (s), medium (m), shoulder (sh).

The chemicals were obtained from ALDRICH Company from Germany and used as such.

3. RESULTS AND DISCUSSION

Let us consider the infrared data of the studied compounds:

L1: ($\nu\text{OH} + \nu\text{NH}$) 2948(br), $\nu\text{as}(\text{COO}^-)$ 1704 (m), 1665 (s), $\nu\text{s}(\text{COO}^-)$ 1321 (m), $\delta(\text{COO}^-)$ 792 (m);

L2: νNH 2987 (br), $\nu\text{as}(\text{COO}^-)$ 1650 (s), $\nu\text{s}(\text{COO}^-)$ 1348 (m), $\delta(\text{COO}^-)$ 796 (m);

A: ($\nu\text{OH} + \nu\text{NH}$) 2972 (br), $\nu\text{as}(\text{COO}^-)$ 1603 (s), $\nu\text{s}(\text{COO}^-)$ 1309 (m), $\delta(\text{COO}^-)$ 799(s);

B: ($\nu\text{OH} + \nu\text{NH}$) 3405 (br), 2976 (br), 2940 (br), $\nu\text{as}(\text{COO}^-)$ 1665 (m), $\nu\text{s}(\text{COO}^-)$ 1240 (m), $\delta(\text{COO}^-)$ 805(m);

C: ($\nu\text{OH} + \nu\text{NH}$) 2985 (br), $\nu\text{as}(\text{COO}^-)$ 1600 (vs), $\nu\text{s}(\text{COO}^-)$ 1315 (m), $\delta(\text{COO}^-)$ 800 (s);

D: ($\nu\text{OH} + \nu\text{NH}$) 3387 (br), 2982 (br), $\nu\text{as}(\text{COO}^-)$ 1608 (s), $\nu\text{s}(\text{COO}^-)$ 1312 (m), $\delta(\text{COO}^-)$ 794 (s);

E: ($\nu\text{OH} + \nu\text{NH}$) 2984 (br), $\nu\text{as}(\text{COO}^-)$ 1633 (sh), 1604 (s), $\nu\text{s}(\text{COO}^-)$ 1315 (m), $\delta(\text{COO}^-)$ 799 (s).

We will just consider the complex-anions for proposing the following structures. From the infrared data we suggest:

- For **A**, a discrete structure with a zinc centre chelated by three anions (Figure 1): the environment around the Zn centre is octahedral.

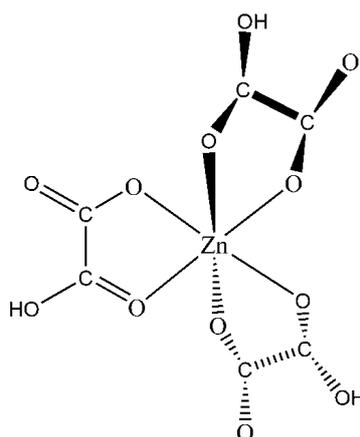
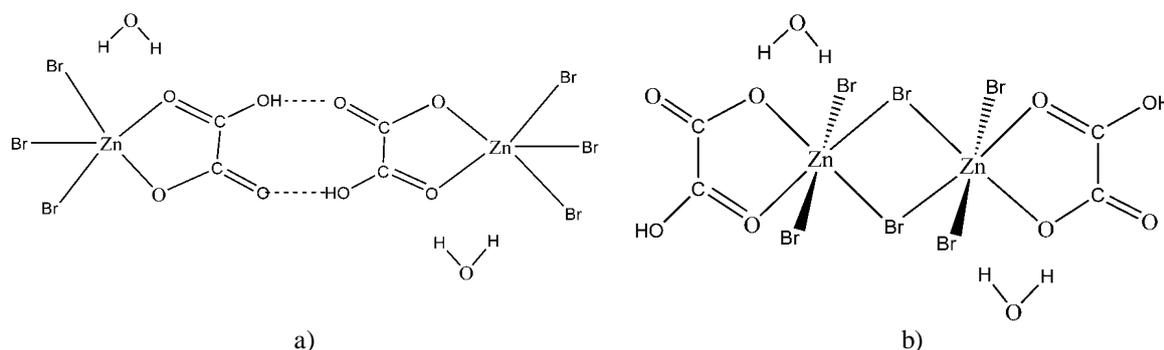


Fig. 1. Proposed structure for **A**.

A hydrogen bonded dimer of the hydrogenoxalate anion has yet been reported by Braga et al [2]. For the first suggested structure we will consider the presence of this dimer and propose:

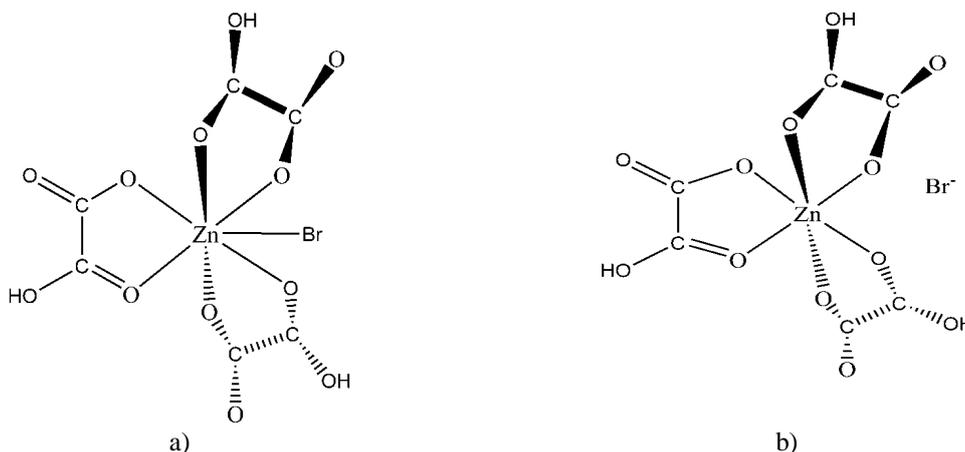
- A first dimeric one with two $[\text{ZnBr}_3]$ monochelated by anions, the environment around the zinc centres being trigonal bipyramidal (Figure 2a).
- A second dimeric structure containing $[\text{Zn}_2\text{Br}_6]^{2-}$ with two bridging bromo atoms chelated by two anions, the environment around the Zn centres being octahedral (Figure 2b).

In these two structures the four water molecules are considered lattice.

Fig. 2. Proposed structures for **B**.

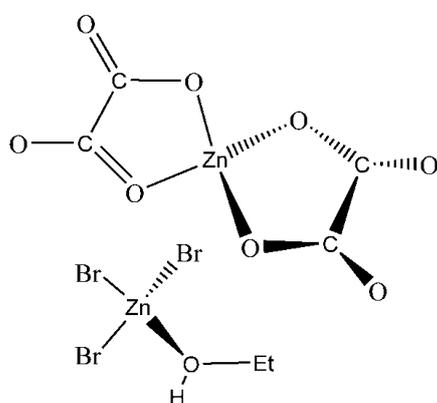
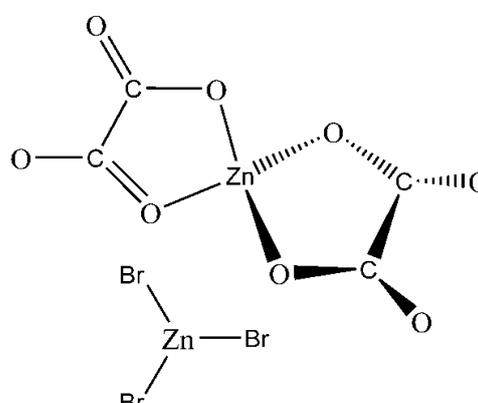
The structure of **C** is deduced from the one of **A** on adding one molecule of Et_3NHBr . Two cases are possible:

- The Br atom coordinates the Zn centre leading to an heptacoordinated Zn centre, a monocapped octahedral environment (Figure 3a).
- The Et_3NHBr molecule is inserted in the holes of the structure of **A** without coordination the zinc centre remaining in an octahedral environment (Figure 3b).

Fig. 3. Proposed structures for **C**.

For **D**, we suggest a structure with two mononuclear metallic components (Figure 4):

- A first metallic component $[\text{Zn}(\text{C}_2\text{O}_4)_2]^{2-}$ with a zinc centre monochelated by two anions, the environment around the Zn centre being tetrahedral.
- The second one being $[\text{ZnBr}_3\text{EtOH}]$ with a tetrahedral environment around the zinc centre.

Fig. 4. Proposed structure for **D**.Fig. 5. Proposed structure for **E**.

The structure of **E** is deduced from the one of **D** on withdrawing the EtOH molecule leading to a trigonal environment around the second component zinc centre (Figure 5).

For all these structures, OH groups and the cation may be considered as involved in hydrogen bonding leading to supramolecular architectures.

4. CONCLUSIONS

The complexes studied in this work have discrete structures with monochelating anions. The environments around zinc centres being trigonal, trigonal bipyramidal, tetrahedral, octahedral or monocapped octahedral. When extra hydrogen bonds are considered, supramolecular architectures may be obtained.

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