

**$\text{Zn}_2(\text{Y})\cdot\text{H}_2\text{O}$, $(\text{Me}_4\text{N})_2\text{H}_2\text{Y}\cdot 3\text{ZnCl}_2$, $(\text{Me}_4\text{N})_4\text{Y}\cdot 5\text{ZnCl}_2\cdot\text{H}_2\text{O}$,
 $(\text{BzNMe}_3)_2\text{H}_2\text{Y}\cdot 2\text{ZnBr}_2$, $\text{Zn}(\text{H}_2\text{Y})\cdot 4\text{ZnCl}_2\cdot 2\text{EtOH}\cdot 14\text{H}_2\text{O}$ AND
 $\text{Zn}(\text{H}_2\text{Y})\cdot 6\text{ZnCl}_2\cdot 2\text{EtOH}\cdot 6\text{H}_2\text{O}$ ($\text{Y} = \text{EDTA}$):
SYNTHESIS AND INFRARED STUDY**

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Abstract: Six acidic or neutral ethylenediaminetetraacetato [H_2Y^{2-} , H_3Y^- or Y^{4-}] containing adducts and derivatives have been synthesized and studied by infrared. The suggested structures are discrete with octahedral or tetrahedral environments around the zinc centres, the ethylenediaminetetraacetic anion behaving as a bichelating, trichelating, tetrachelating and hydrogen bonds involved, pentachelating or hexachelating and hydrogen bonds involved ligand. For most of the structures when intermolecular hydrogen bonds are considered, a supramolecular architecture is obtained.

Keywords: *anion, discrete structures, polychelating and hydrogen bonds involved, supramolecular architectures*

INTRODUCTION

The main results on the coordination ability of oxyanions have been summarized by Hathaway [1]. Our group interested by the coordinating ability of oxyanions has yet reported several papers [2 – 11]. We report here the study of the interactions between $[\text{Me}_4\text{N}][\text{H}_3\text{Y}]\cdot\text{H}_2\text{O}$, $[\text{Et}_4\text{N}][\text{H}_3\text{Y}]\cdot 3\text{H}_2\text{O}$ or $[\text{BzN}(\text{CH}_3)_2][\text{H}_2\text{Y}]\cdot\text{H}_2\text{O}$ and ZnCl_2 or ZnBr_2 which has yielded six new compounds, infrared study of which have been carried out then structures suggested on the basis of spectroscopic data.

MATERIALS AND METHODS

$[\text{Me}_4\text{N}][\text{H}_3\text{Y}]\cdot\text{H}_2\text{O}$ (L_2), $[\text{Et}_4\text{N}][\text{H}_3\text{Y}]\cdot 3\text{H}_2\text{O}$ (L_4) and $[\text{BzNMe}_3]_2[\text{H}_2\text{Y}]\cdot\text{H}_2\text{O}$ (L_5) have been obtained as powders after the water evaporation of the solution obtained on dissolving ethylenediaminetetraacetic acid (EDTA) in an aqueous solution of Me_4NOH , Et_4NOH or BzMe_3NOH in 1:4 ratio. The analytical data % calculated (% found) (L_2): C = 43.86 (43.14), H = 7.62 (7.27), N = 10.96 (10.33); (L_4): C = 45.46 (46.07), H = 8.69 (8.75), N = 8.84 (8.88); (L_5): C = 59.19 (59.07), H = 7.95 (7.87), N = 9.20 (9.23) have allowed to suggest the formulae for (L_2), (L_4) and (L_5). When ZnCl_2 or ZnBr_2 are allowed to react with L_2 , L_4 or L_5 in specific ratios, white precipitates are obtained which are stirred around two hours and washed with ethanol:

- ZnBr_2 with L_5 in 6:1 ratio gives (**A**)
- ZnCl_2 with L_2 in 4:1 ratio gives (**B**)
- ZnCl_2 with L_2 in 3:1 ratio gives (**C**)
- ZnBr_2 with L_5 in 4:1 ratio gives (**D**)
- ZnCl_2 with L_4 in 1:1 ratio gives (**E**)
- ZnCl_2 with L_4 4:1 ratio gives (**F**)

The analytical data % calculated (% found) have allowed to suggest the following formulae for the six new compounds (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	$\text{Zn}_2[\text{Y}]\cdot\text{H}_2\text{O}$	27.48	27.9	3.23	3.63	6.41	6.39
B	$(\text{Me}_4\text{N})_2[\text{H}_2\text{Y}]\cdot 3\text{ZnCl}_2\cdot\text{H}_2\text{O}$	24.98	25.01	4.66	5.12	6.47	6.54
C	$[\text{Me}_4\text{N}]_4\text{Y}\cdot 5\text{ZnCl}_2\cdot\text{H}_2\text{O}$	24.32	24.5	4.87	5.12	6.54	6.20
D	$[\text{BzNMe}_3]_2[\text{H}_2\text{Y}]\cdot 2\text{ZnBr}_2$	34.61	34.8	4.45	4.75	5.38	4.92
E	$\text{Zn}[\text{H}_2\text{Y}]\cdot 4\text{ZnCl}_2\cdot 2\text{EtOH}\cdot 14\text{H}_2\text{O}$	13.53	13.61	4.22	3.61	2.25	2.23
F	$\text{Zn}(\text{H}_2\text{Y})\cdot 6\text{ZnCl}_2\cdot 2\text{EtOH}\cdot 6\text{H}_2\text{O}$	12.26	12.35	2.65	2.79	2.04	2.04

The infrared spectra were recorded by a Bruker FTIR (4400 – 350 cm^{-1}) spectrometer (Saint Boniface College, Canada), the sample being as Nujol mulls while CsI windows were used. The elemental analyses have been performed at the laboratory of Microanalyses at the University of Bath (UK). Infrared data are given in cm^{-1} [IR abbreviations: (br) broad, (vs) very strong, (s) strong, (m) medium, (sh) shoulder].

All the chemicals are from Aldrich Company and were used without any further purification.

RESULTS AND DISCUSION

Let us consider the infrared data of the studied derivatives based on assignment in [12]:

A: $\nu_{\text{as}}(\text{COO}) = 1638 \text{ s}$; $\delta(\text{CH}_2) + \nu_{\text{s}}(\text{COO}) = 1435 \text{ sh}$, 1324 w ; $\nu(\text{CC}) = 893 \text{ sh}$;

B: $\nu(\text{NH}) = 3023 \text{ sh}$; $\nu_{\text{as}}(\text{COO}) + \delta(\text{NH}) = 1632 \text{ s}$, 1615 sh ; $\delta(\text{CH}_2) + \nu_{\text{s}}(\text{COO}) = 1495 \text{ s}$, 1360 s ; $\nu(\text{CC}) = 927 \text{ sh}$;

C: $\nu_{\text{as}}(\text{COO}) = 1602 \text{ s}$, 1583 w ; $\delta(\text{CH}_2) + \nu_{\text{s}}(\text{COO}) = 1435 \text{ sh}$, 1385 s ; $\nu(\text{CC}) = 867 \text{ w}$;

(D): $\nu_{\text{as}}(\text{COO}) + \delta(\text{NH}) = 1624 \text{ s}$, 1565 sh ; $\delta(\text{CH}_2) + \nu_{\text{s}}(\text{COO}) = 1410 \text{ s}$, 1315 sh ; $\nu(\text{CC}) = 876 \text{ vs}$;

E: $\nu(\text{OH}_2) + \nu(\text{NH}) = 3425 \text{ s}$; $\nu_{\text{as}}(\text{COO}) + \delta(\text{NH}) = 1612 \text{ sh}$, 1504 w ; $\delta(\text{CH}_2) + \nu_{\text{s}}(\text{COO}) = 1416 \text{ sh}$, 1355 s ; $\nu(\text{CC}) = 947 \text{ w}$;

F: $\nu(\text{OH}_2) + \nu(\text{NH}) = 3412 \text{ s}$; $\nu_{\text{as}}(\text{COO}) + \delta(\text{NH}) = 1648 \text{ s}$, 1559 sh ; $\delta(\text{CH}_2) + \nu_{\text{s}}(\text{COO}) = 1428 \text{ s}$, 1345 s ; $\nu(\text{CC}) = 867 \text{ w}$.

From these data we suggest six discrete structures with the ethylenediaminetetraacetic anion behaving as a bichelating, trichelating, tetrachelating and hydrogen bonds involved, pentachelating- or hexachelating and hydrogen bonds involved ligand the environment of zinc being tetrahedral or octahedral.

For **A** a dimeric structure is suggested with tetrahedral environment around zinc centres, the anion behaving as a tetrachelating ligand, the water molecules being considered lattice (Figure 1.)

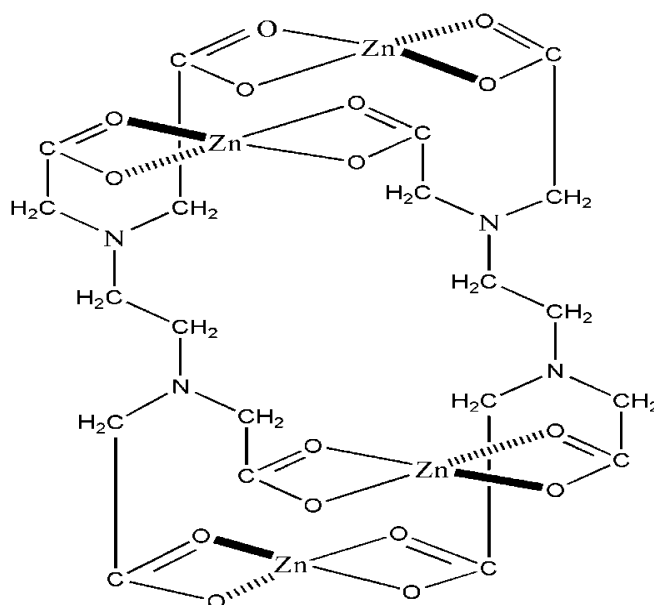


Figure 1. Proposed structure for the compound A

For **B** a discrete structure with tetrahedral zinc centres is suggested, the anion behaving as a trichelating ligand (Figure 2).

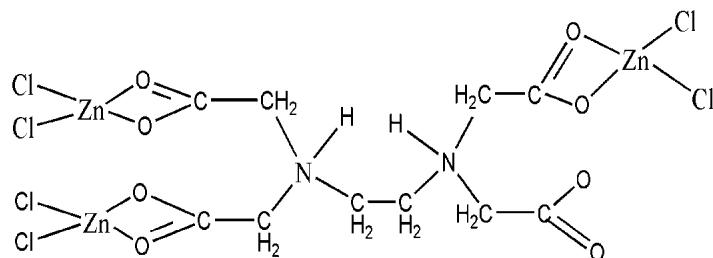


Figure 2. Proposed structure for the compound **B**

For **C** a discrete structure is proposed with tetrahedral zinc centres, the anion behaving as a pentachelating ligand, the water being considered as lattice (Figure 3).

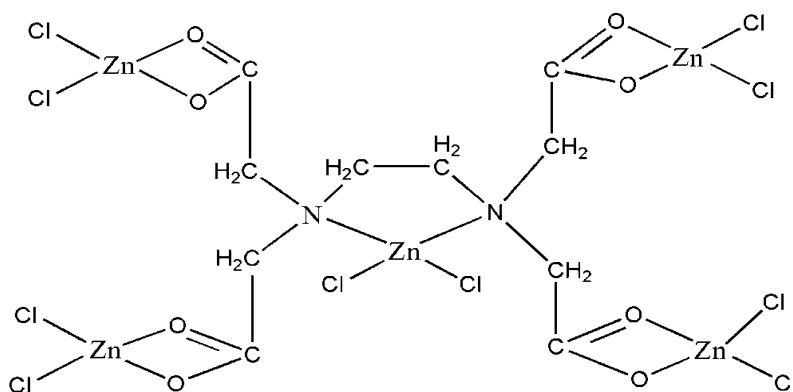


Figure 3. Proposed structure for the compound **C**

For **D** is suggested a discrete structure with tetrahedral zinc centres, the anion acting as a bichelating ligand (Figure 4.)

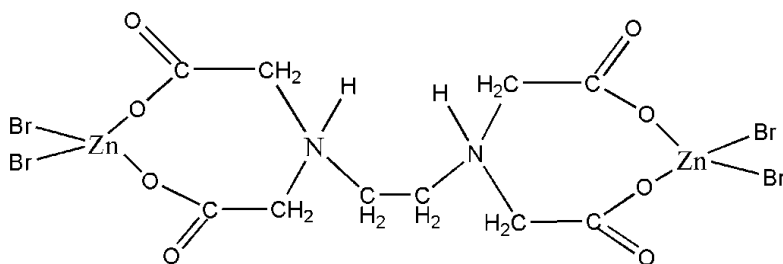


Figure 4. Proposed structure for the compound **D**

For **E** a two components structure is suggested: one consists of an acidic anion tetrachelating four ZnCl_2 molecules, two EtOH molecules being connected to $[\text{H}_2\text{Y} \cdot 4\text{ZnCl}_2 \cdot 8\text{H}_2\text{O}]^{2-}$ trough $\text{NH} \cdots \text{O}$ hydrogen bonds and the second being $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ (Figure 5).

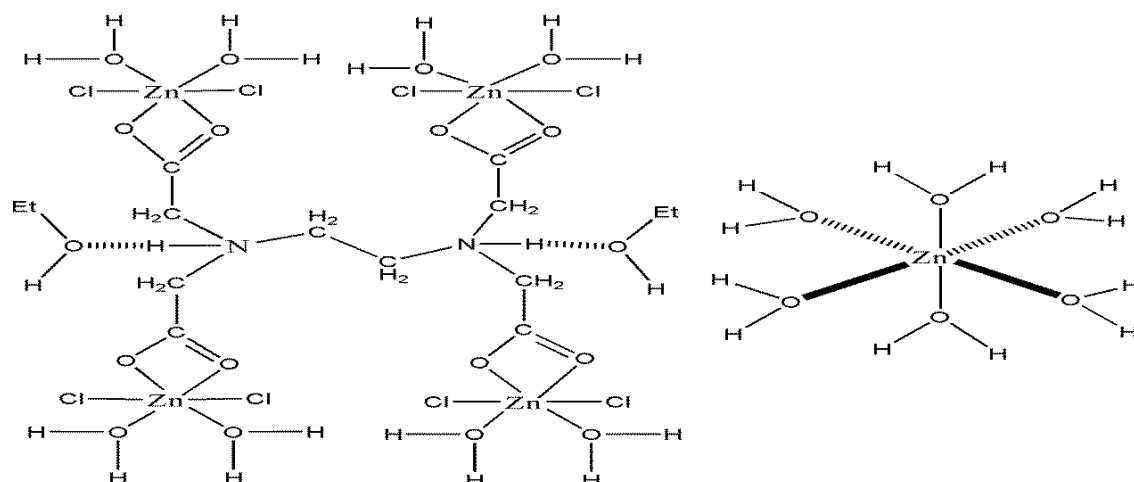


Figure 5. Proposed structure for the compound **E**

For **F** a two components structure is suggested: one consists of an acidic anion hexachelating six $ZnCl_2$ molecules, two $EtOH$ molecules being connected to $[H_2Y \cdot 6ZnCl_2]^{2-}$ through $NH \cdots O$ hydrogen bonds and the second being $[Zn(H_2O)_6]^{2+}$ (Figure 6).

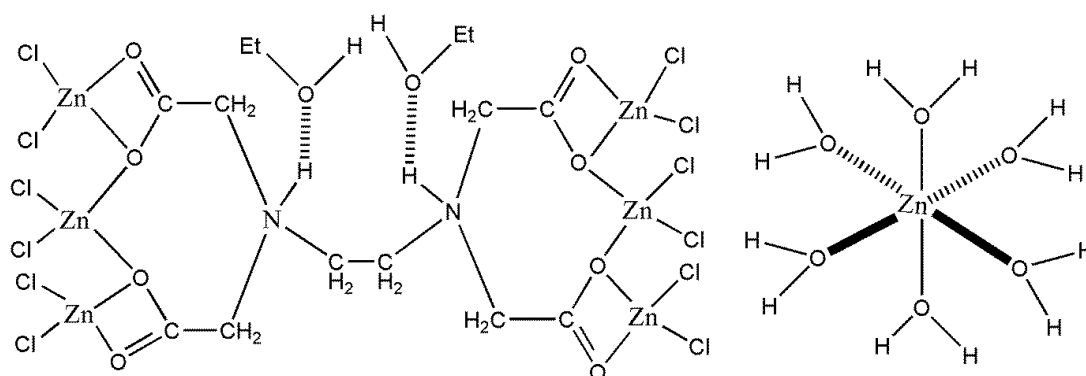


Figure 6. Proposed structure for the compound **F**

For all these structures except **A** and **C** when NH groups are involved in extra hydrogen bonds, a supramolecular architecture may be obtained.

CONCLUSION

The structures of six compounds studied in this work have a discrete structure with octahedral or tetrahedral environments around the zinc centres, the anion behaving as a bichelating; trichelating, tetrachelating and hydrogen bonds involved pentachelating or hexachelating and hydrogen bonds involved ligand. For all these structures except **A** and **C** when intermolecular hydrogen bonds are considered, a supramolecular architecture may be obtained.

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