

NEW MX_2 OXALATO POLYNUCLEAR ADDUCTS (M = Cd, Hg, Zn; X = Cl, Br): SYNTHESIS AND INFRARED STUDY

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Abstract: Nine mono-, di- and trinuclear MX_2 oxalato adducts have been synthesized, their infrared study carried out. The suggested structures are ionic, the oxalate anion behaving as a chelating ligand. Cage structures, when non symmetrical cations are involved, have been suggested.

Keywords: *cage, ionic structures, polychelating oxalate*

INTRODUCTION

While oxalato adducts with SnX_4 [1] or ReCl_4 [2] have been reported, oxalato complex-anions such as $[\text{Cu}(\text{C}_2\text{O}_4)_2\cdot\text{H}_2\text{O}]^{-2}$ [3], $[\text{Cu}(\text{C}_2\text{O}_4)_2\cdot 2\text{H}_2\text{O}]^{-2}$ [4] with a complete substitution of the halides are more numerous. Our group has yet published results dealing with oxalato adducts and derivatives [5]. In this work dealing with the coordination ability of the oxalate anion, for avoiding the substitution of the halide leading to derivatives, we have initiated the study of the interactions between quaternary ammonium oxalic acid salts with an excess of metal halides which has yielded nine new MX_2 adducts, infrared study of which have been carried out, and structures suggested on the basis of infrared data.

EXPERIMENTAL

$(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ have been synthesized as yet reported [5].

$[(i\text{Bu})_2\text{NH}_2]_2\text{C}_2\text{O}_4$ has been obtained as a precipitate on neutralizing oxalic acid with $i\text{Bu}_2\text{NH}$ in water.

$(\text{Et}_4\text{N})_2\text{ZnCl}_4$ and $(\text{Et}_4\text{N})_2\text{CdCl}_4$ have been obtained on mixing ethanolic solutions of ZnCl_2 or $\text{CdCl}_2\cdot 6\text{H}_2\text{O}$ with an excess of $\text{Et}_4\text{NCl}\cdot\text{H}_2\text{O}$. The solutions obtained, when submitted to a slow solvent evaporation, give powders.

When ethanolic solutions of $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, are mixed in 1:2 ratio (for **A**, **B**, **D**) or 1:4 ratio (for **C**, **E**, **F**), with MX_2 , precipitates are obtained.

When ethanolic solutions of $(i\text{Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4$, $(\text{Et}_4\text{N})_2\text{ZnCl}_4$, $(\text{Et}_4\text{N})_2\text{CdCl}_4$ or ZnCl_2 are mixed in ratios 4:1, 1:4 and 1:1, precipitation occurs.

Elemental analyses of **A – I** compounds has allowed suggesting the following formulae [% calc (% found)]:

- [**A**] $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{CdCl}_2$: C = 19.90 (19.33); H = 3.98 (3.65); N = 4.64 (4.40);
Cl = 23.55 (21.78); Cd = 37.29 (36.34);
- [**B**] $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{CdBr}_2$: C = 15.37 (15.38); H = 3.07 (3.33); N = 3.58; (3.60);
Br = 45.54 (42.64); Cd = 32.03 (31.30);
- [**C**] $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{HgCl}_2$: C = 15.40 (15.61); H = 3.08 (3.01); N = 3.59 (3.52);
Cl = 18.22 (16.78); Hg = 51.48 (51.28);
- [**D**] $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{HgBr}_2$: C = 12.53 (12.49); H = 2.50 (2.45); N = 2.92 (2.86);
Hg = 41.91 (41.21);
- [**E**] $(\text{Et}_4\text{N})_2\text{C}_2\text{O}_4\cdot 2\text{CdCl}_3\text{NEt}_4\cdot\text{H}_2\text{O}$: C = 37.72 (37.69); H = 7.82 (7.75);
N = 5.18 (4.17);
- [**F**] $2(\text{Et}_4\text{N})_2\text{C}_2\text{O}_4\cdot 3\text{ZnCl}_2\cdot\text{Et}_4\text{NCl}$: C = 40.43 (41.93); H = 8.08 (8.05);
N = 5.61 (5.32);
- [**G**] $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 3\text{CdBr}_2$: C = 11.40 (11.34); H = 2.28 (2.40); N = 2.66 (2.51);
Br = 45.54 (42.62); Cd = 32.03 (31.30);
- [**H**] $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4\cdot 3\text{HgBr}_2$: C = 9.10 (8.62); H = 1.82 (1.67); N = 2.12 (1.79);
Hg = 45.71 (45.95);
- [**I**] $(i\text{Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4\cdot 2\text{ZnC}_2\text{O}_4\cdot \frac{1}{4}i\text{Bu}_2\text{NH}_2\text{Cl}$: C = 41.95 (42.2); H = 6.55 (8.40);
N = 4.59 (4.47).

All the precipitates were stirred no less than two hours, filtered and washed by hot ethanol. Infrared spectra have been obtained by means of a Bruker FTIR or a 580PE spectrometer, the sample being as Nujol mull, using CsI windows; infrared data are given in cm⁻¹ [abbreviations: (vs) very strong, (s) strong, (m) medium, (w) weak]. The elemental analyses have been performed by the CNRS «Service Central d'Analyses» Vernaison, France, the Laboratory of Microanalyses, Department of Chemistry, University of Padova, Italy and the Microanalyses Laboratory, Department of Chemistry, University of Bath, UK.

RESULTS AND DISCUSSION

Let us considering the infrared data of the synthesized adducts:

- [A] $\nu\text{asCOO}^- = 1645\text{vs} - 160\text{vs}$, $\nu\text{sCOO}^- = 1305\text{s}$, $\delta\text{COO}^- = 794\text{s}$;
- [B] $\nu\text{asCOO}^- = 1660\text{vs} - 1608\text{vs}$, $\nu\text{sCOO}^- = 1313\text{m}$, $\delta\text{COO}^- = 794\text{s}$;
- [C] $\nu\text{asCOO}^- = 1602\text{vs}$, $\nu\text{sCOO}^- = 1277\text{vs}$, $\delta\text{COO}^- = 779\text{s}$;
- [D] $\nu\text{asCOO}^- = 1602\text{vs}$, $\nu\text{sCOO}^- = 1269\text{s}$, $\delta\text{COO}^- = 777\text{s}$;
- [E] $\nu\text{asCOO}^- = 1624\text{vs}$, $\nu\text{sCOO}^- = 1312\text{s}$, $\delta\text{COO}^- = 790\text{vs}$;
- [F] $\nu\text{asCOO}^- = 1609\text{vs}$, $\nu\text{sCOO}^- = 1311\text{s}$, $\delta\text{COO}^- = 797\text{vs}$;
- [G] $\nu\text{asCOO}^- = 1609\text{vs}$, $\nu\text{sCOO}^- = 1311\text{s}$, $\delta\text{COO}^- = 797\text{vs}$;
- [H] $\nu\text{asCOO}^- = 1624\text{vs}$, $\nu\text{sCOO}^- = 1312\text{s}$, $\delta\text{COO}^- = 790\text{vs}$;
- [I] $\nu\text{asCOO}^- = 1609\text{vs}$, $\nu\text{sCOO}^- = 1316\text{s}$, $\delta\text{COO}^- = 820\text{w}$.

(Me₄N)₂C₂O₄·2CdX₂ (X = Cl, Br) [A, B]

The presence of νasCOO^- as two very strong bands and νsCOO^- as a very strong band are indications of the presence of a non centrosymmetrical oxalate according to Group Theory [6]. While considering a tetrahedral environment around Cd as predicted by Ligand Field Theory, we suggest the ionic structure containing a dinuclear complex-anion with an asymmetrically bichelating oxalate, reported in Figure 1.

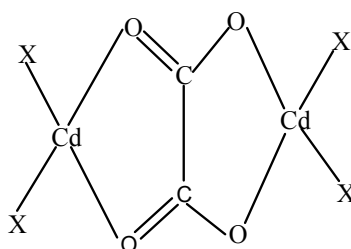


Figure 1. Structure proposed for *A* and *B* compounds

(Me₄N)₂C₂O₄·2HgX₂ (X = Cl, Br) [C, D]; (Et₄N)₂C₂O₄·2CdCl₃NEt₄·H₂O [E]; 2(Et₄N)₂C₂O₄·3ZnCl₂·Et₄NCl [F]

The presence of only two stretching bands due to νCOO^- groups in **C**, **D**, **E** and **F** indicates the presence of a centrosymmetrical oxalate according to Group Theory [6]

and allow suggesting an ionic structure containing dinuclear complex-anions with symmetrically chelating oxalate, reported on Figure 2. In **E**, HgCl_2 is replaced by $[\text{CdCl}_3 \cdot \text{H}_2\text{O}]^-$ and Me_4N^+ by Et_4N^+ .

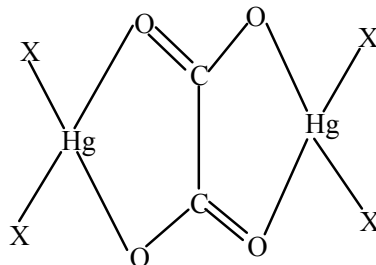


Figure 2. Ionic structure containing dinuclear complex-anions with symmetrically chelating oxalate

In the case of **F** one $[\text{C}_2\text{O}_4(\text{ZnCl}_2)_2]^{2-}$ anion and one $[\text{C}_2\text{O}_4(\text{ZnCl}_3)]^{3-}$ are in electrostatic interactions with the tetraethylammonium cation (Figure 3). This adduct can be considered as a 1:1 adduct between $(\text{Et}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{ZnCl}_2$ and $(\text{Et}_4\text{N})_3\text{C}_2\text{O}_4 \cdot \text{ZnCl}_3$: it appears as an insertion adduct.

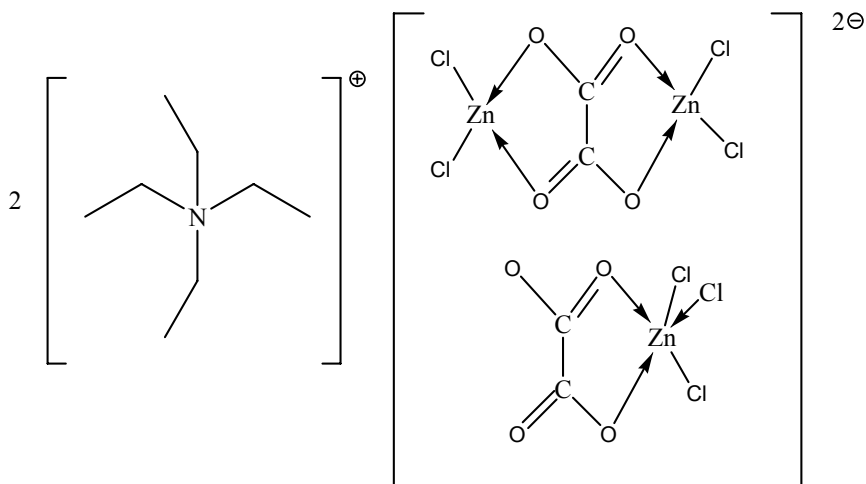


Figure 3. Structure proposed for compound **F**

$(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 3\text{MBr}_2$ ($\text{M} = \text{Cd}, \text{Hg}$) [**G**, **H**]

In the case of the mercury adduct the small splitting of the stretching bands allows to consider a centrosymmetrical oxalate. An almost similar splitting of the stretching bands widening them is observed on the IR spectrum of the cadmium adduct and allow to conclude to the presence of a centrosymmetrical oxalate; we therefore consider for **G** and **H** a dimer in which the two dinuclear anions $[\text{C}_2\text{O}_4(\text{MX}_2)_2]^{2-}$ are connected through the third MX_2 located at the center of the faces of a parallelepiped involving octahedral or tetrahedral environments; the oxalate anion is a tetrachelating ligand (Figure 4).

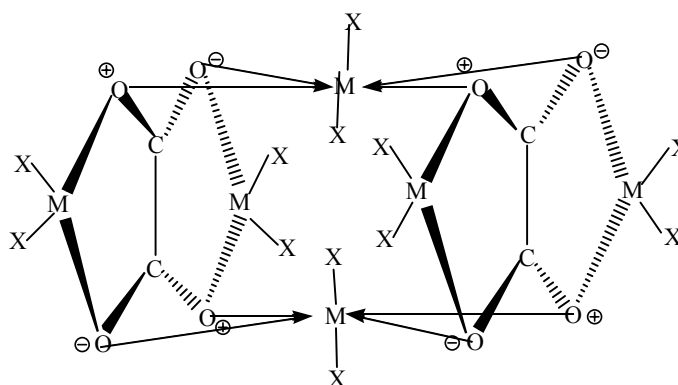


Figure 4. Structure proposed for **G** and **H** compounds

$(i\text{Bu}_2\text{NH}_2)_2\text{C}_2\text{O}_4 \cdot 2\text{ZnC}_2\text{O}_4 \cdot i\text{Bu}_2\text{NH}_2\text{Cl}$ [I**]**

The presence of the two bands in the stretching region indicates a centrosymmetrical oxalate according to Group Theory [6] and allows suggesting a structure containing a central bichelating oxalate and two external monochelating ones, the environment around zinc being tetrahedral. The cation when involved through N-H...O hydrogen bonds lead to a supramolecular architecture (Figure 5). We arbitrary report the dimer which has a cage structure – the N-H...O hydrogen bonds involving the diisobutylammonium cations are responsible of the wide and strong absorption around 3300 cm^{-1} on the infrared spectrum.

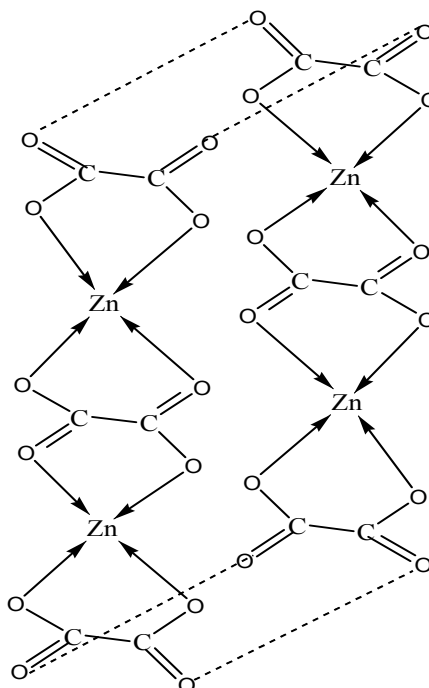


Figure 5. Structure proposed for compound **I**

CONCLUSION

While the symmetrical cations have led to ionic structures with a polychelating oxalate in electrostatic interactions with the cations, the introduction of a non symmetrical cation has allowed obtaining supramolecular structures involving the cations through NH...O hydrogen bonds.

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