

## A NEW SYNTHETIC ROUTE FOR POLYNUCLEAR OXALATO ADDUCTS

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**ABSTRACT.** A new synthetic route for new oxalato polynuclear adducts has been described and structures suggested on the basis of their infrared spectra.

## INTRODUCTION

$(SnX_4)_2C_2O_4(NEt_4)_2$  ( $X = Cl, Br, I$ ) have been synthesized by Skapski et. al. [1] who determined their X-ray structure while Le Floch et. al. [2] carried out the spectroscopic study using X-ray results: the structure consists of an oxalate bichelating two  $SnX_4$  molecules with two entities per unit cell. Scott et. al. [3] reported the synthesis of binuclear, trinuclear, tetranuclear cobalt(III) oxalato complexes while Urts [4,5] obtained some oxalato amine complexes of Ni(II), Cu(II) and Zn(II). This paper which is the continuation of the research carried out in our laboratory on oxoanions acting as ligands [6,7], deals with a new and facile route to obtain polynuclear oxalato adducts, structures of which are suggested on the basis of the infrared spectra.

## EXPERIMENTAL

$(Me_4N)_2C_2O_4 \cdot 2H_2O$  was obtained by mixing stoichiometric amounts of a  $Me_4NOH$  10% water solution with oxalic acid; slow evaporation gave a white powder recrystallized from absolute ethanol. When  $Et_4NOH$  as a 20% water solution was used, hygroscopic  $(Et_4N)_2C_2O_4 \cdot 4H_2O$  was obtained.

On mixing  $MX_n$  ( $n = 2, 3$ ;  $X = Cl, Br$ ;  $M = Cd, Cu, Co, Mn, Sb, Bi$ ) as absolute ethanolic solutions in ratio 1:2, 1:3 or 1:4 (reported in parentheses) with ethanolic solutions of  $(R_4N)_2C_2O_4 \cdot nH_2O$  ( $R = Me$  or  $Et$ ;  $n = 2$  or  $4$ ), precipitation occurs. After stirring for about one or two hr the precipitate is collected and dried under vacuum.

**Analytical data.** % calculated (% found)  $(CdCl_2)_2(Me_4N)_2C_2O_4(1:2)$  C 19.91 (19.33); H 3.98 (3.90); N 4.64 (4.40); Cl 23.55 (23.48).  $(CuCl_2)_2(Me_4N)_2C_2O_4 \cdot H_2O(1:2)$ : C 22.94 (22.22); H 4.97 (4.57); N 5.35 (5.23); Cl 27.15 (27.69).  $(CuBr_2)_2(Me_4N)_2C_2O_4 \cdot H_2O(1:2)$ : C 17.12 (17.14); H 3.71 (3.56); N 3.99 (3.84); Br 45.61 (45.27).  $(CoCl_2)_2(Me_4N)_2C_2O_4 \cdot 4H_2O$  1/4 EtOH(1:2): C 21.74 (21.12); H 5.78 (5.44); N 4.83 (4.79); Cl 24.50 (24.00).  $(MnCl_2)_2(Me_4N)_2C_2O_4 \cdot 4H_2O$  3/4 EtOH(1:2): C 23.13 (23.52); H 6.12 (5.70); N 4.69 (5.03); Cl 23.81 (23.45).  $(SbCl_3)_2(Me_4N)_2C_2O_4(1:2)$ : C 17.32 (16.67); H 3.46 (3.86); N 4.04 (4.24); Cl 31.75 (30.66).  $(BiCl_3)_2C_2O_4(1:2)$  C 13.28 (13.06); H 3.10 (2.76); N 3.10 (2.95); Cl 23.58 (24.04).  $(CdBr_2)_3(Me_4N)_2C_2O_4(1:3)$ : C 13.90 (13.85); H 2.94 (2.98); N 2.49 (2.51); Br 42.79 (42.39).  $(HgCl_2)_4(Me_4N)_2C_2O_4(1:4)$ : C 8.95 (8.87); H 1.94 (1.80); N 2.08 (2.03); Cl 21.48 (22.00).

The elemental analyses were performed by the analytical laboratory of the department of chemistry (University of Padova, Italy) and the "Service Central d'Analyses", C.N.R.S. (Vernaison, France). The infrared spectra were scanned as nujol mulls on a 580 PE or Bruker FTIR model FS 113 V spectrophotometer.

## RESULTS AND DISCUSSION

*Binuclear adducts.* On Table 1 are reported partial infrared data of the binuclear adducts, the assignments being made using those of Le Floch et. al. [2].

A1	A2	A3	A4	A5	A6	A7	Assignment
1616 v.s	1634 v.s	1608 s	1622 v.s	1676 s 1609 s	1615 s	1608 v.s	$\nu$ as COO <sup>-</sup>
1326 s	1363 s		1361 m	1366 m	1339 w		
1312 sh	1329 m	1316 m	1317 s		1290 s	1289 m	$\nu$ s COO <sup>-</sup>
201 s	288 s	216 s	295 s	280 v.s	259 s	244 s	$\nu$ MX
248 w	233 w		240 w	246 w			$\nu$ MO

v s = very strong; s = strong; m = medium; w = weak; sh = shoulder.

The frequencies are in cm<sup>-1</sup>.

A1 = (CdCl<sub>2</sub>)<sub>2</sub>(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>; A2 = (CuCl<sub>2</sub>)<sub>2</sub>(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O;

A3 = (CuBr<sub>2</sub>)<sub>2</sub>(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O; A4 = (CoCl<sub>2</sub>)<sub>2</sub>(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.4H<sub>2</sub>O  
1/4 EtOH;

A5 = (MnCl<sub>2</sub>)<sub>2</sub>(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.4H<sub>2</sub>O 3/4 EtOH;

A6 = (SbCl<sub>3</sub>)<sub>2</sub>(Me<sub>4</sub>N)<sub>2</sub>C

While considering the oxalate anion we expect for stretching bands; when the oxalate belongs to D<sub>2h</sub> point group two stretching vibrations are infrared active; when the point group is C<sub>2v</sub>, C<sub>s</sub> or C<sub>1</sub> the four stretching bands appear. Because of the appearance of two carboxylato stretching bands in the IR spectrum we can reasonably conclude the presence of D<sub>2h</sub> point group for the oxalate as Scott et. al. [3] reported for their tetranuclear Co(III) complexes.

In (SnX<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>(NEt<sub>4</sub>)<sub>2</sub> adducts containing a bichelating oxalate, Le Floch et. al. localized three bands due to COO<sup>-</sup> (the three bands can be explained by solid state effects); Lahlou and Diop [7] in (SnPh<sub>3</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> mentioned the presence of three bands due to COO<sup>-</sup> and conclude the presence of a bichelating oxalate.

From the similarities with well established bichelating oxalato containing complexes (two or three bands due to COO<sup>-</sup>) we can suggest for these binuclear adducts a discrete structure containing a bichelating oxalate (Fig. 1).

*Tri and tetranuclear adduct.* The IR spectrum of (CdBr<sub>2</sub>)<sub>3</sub>(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> exhibits two bands at 1660 cm<sup>-1</sup> (strong) and 1312 cm<sup>-1</sup> (strong) while that of (HgCl<sub>2</sub>)<sub>4</sub>(Me<sub>4</sub>N)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> exhibits two bands at 1578 cm<sup>-1</sup> (strong) and 1304 cm<sup>-1</sup> (strong). These bands are assigned to as COO<sup>-</sup> and s COO<sup>-</sup> respectively. From these spectral data we conclude that the oxalate compound will assume a D<sub>2h</sub> symmetry. This will eliminate for the cadmium adduct the discrete structure containing a tri unidentate oxalate because of C<sub>s</sub> symmetry and suggest the structure reported in Fig. 2. This type of tetradentate oxalate (bi unidentate and monochelate) has never been reported earlier.

For the mercury adduct two structures are consistent with the spectral data: a tetra unidentate oxalate containing structure as in the tetranuclear Co(III) complexes (Fig. 3a) and a tetrachelating D<sub>2h</sub> symmetry oxalate containing structure (Fig. 3b).



Fig. 1.  $2MX_n \cdot C_2O_4(Me_4N)_2$ M = Cd, Cu, Co, Mn, Sb, Bi,  $n=2,3$ 

X = Cl, Br.

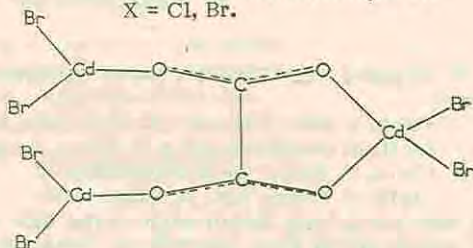
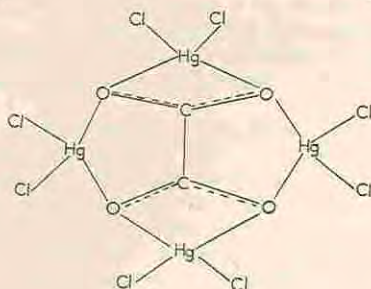
Fig. 2.  $3CdBr_2 \cdot C_2O_4(Me_4N)_2$ 

Fig. 3a.

Fig. 3b.  $4HgCl_2 \cdot C_2O_4(Me_4N)_2$ 

In the new titled adducts reported in this paper the great tendency of the oxalate anion to chelation has been confirmed. The particular behaviour of the oxalate in tri and tetranuclear adducts has been established.

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