

HOMO AND HETEROPOLYNUCLEAR NEW OXALATOORGANOTIN (IV) ADDUCTS. AN INFRARED AND MÖSSBAUER STUDY

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Abstract: Six new oxalato homo (Sn only) and hetero (Sn, Cd, Sb) polynuclear adducts have been obtained on allowing $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ to react with SnPh_2Cl_2 or $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)\text{SnPh}_2 \cdot \text{H}_2\text{O}$ to react with SnPh_2Cl_2 , SnMe_2Cl_2 , CdCl_2 , $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ or SbCl_3 in specific ratio. The obtained adducts have been studied by elemental analyses and infrared spectroscopy and structures suggested on the basis of the spectroscopic data.

Keywords: *homo- and heteropolynuclear adducts, infrared, mono- and bichelating oxalate*

INTRODUCTION

The various applications found with molecules belonging to organotin (IV) family – antibacterial, cardio-vascular and anti-malarial properties and industrial uses explains why many groups have been and are still involved in synthesizing new molecules of this family, expecting some possibilities of applications [1 – 11].

Our group has yet reported several papers dealing with [12] and initiates here the study of the interactions between $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ or $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)\text{SnPh}_2 \cdot \text{H}_2\text{O}$ with SnPh_2Cl_2 , SnMe_2Cl_2 , CdCl_2 , $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ and SbCl_3 which have yielded six new adducts, infrared studies of which have been carried out and structures suggested on the basis of spectroscopic data.

EXPERIMENTAL

$(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)2\text{SnPh}_2 \cdot \text{H}_2\text{O}$ (**L**₁) has been obtained on mixing $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (**L**₂) with SnPh_2Cl_2 as ethanolic solution in 2/1 ratio.

When $(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4)2\text{SnPh}_2 \cdot \text{H}_2\text{O}$ and SnMe_2Cl_2 , CdCl_2 , $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ or SbCl_3 in ethanol are mixed in specific ratios, precipitation occurs. The precipitate were stirred no less than two hours, filtered and washed with hot ethanol. The analytical data reported below - with the ratios salt/halide between brackets - have allowed to suggest the following formulas [% calculated (% found)]:

$2(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4) \cdot \text{SnPh}_2\text{C}_2\text{O}_4 \cdot \text{CdC}_2\text{O}_4 \cdot 3\text{CdCl}_2$

(A) [1**L**₁/2]:

C = 26.18 (27.42); H = 3.75 (3.60); N = 3.59 (3.40); Cl = 13.64 (14.40); Sn = 7.61 (8.72); Cd = 28.82 (28.06);

$(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4) \cdot 2\text{SnPh}_2\text{C}_2\text{O}_4 \cdot 2\text{SbCl}_3$

(B) [2**L**₁/1]: C = 31.10 (31.50); H = 3.19 (3.62); N = 1.88 (2.01); Cl = 15.30 (15.32); Sn = 15.97 (15.91); Sb = 17.08 (17.83);

$2[(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4] \cdot \text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 2\text{SnPh}_2\text{Cl}_2$

(C) [1**L**₂/1**SnPh**₂**Cl**₂]: C = 39.62 (40.15); H = 4.71 (4.65); N = 3.85 (3.67); Cl = 9.75 (9.55); Sn = 24.48 (24.19);

$(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4) \cdot 2\text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 2\text{SnPh}_2\text{Cl}_2$

(D) [1**L**₁/2**SnMe**₂**Cl**₂]: C = 33.31 (33.63); H = 2.90 (3.01); N = 1.85 (1.78); Cl = 9.38 (9.39); Sn = 31.38 (31.95);

$(\text{Me}_4\text{N})_6\text{SnPh}_2(\text{C}_2\text{O}_4)_4 \cdot 4[\text{SnPh}_2(\text{C}_2\text{O}_4)\text{CdBr}_2]$

(E) [1**L**₁/2**CdBr**₂·4**H**₂**O**]: C = 31.51 (33.27); H = 3.51 (3.06); N = 2.40 (1.96); Br = 18.23 (17.57); Sn = 16.93 (16.48); Cd = 12.82 (12.62);

$3(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot \text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 3\text{SnPh}_2\text{Cl}_2 \cdot 2\text{SnPhCl}_3$

(F) $[\text{1L}_1/3\text{SnPh}_2\text{Cl}_2]$ C = 37.31 (37.75); H = 4.28 (4.33); Cl = 16.12 (16.15); N = 3.18 (3.14); Sn = 26.98 (27.29).

The elemental analyses were performed by the CNRS “Service Central d’Analyses”, Vernaison, France, the IR spectra at the University of Padova, using a PE 580 and a Bruker FTIR spectrometer, the sample being as a Nujol mull, using CsI or polyethylene as optical windows. The infrared data are given in cm^{-1} and the Mössbauer ones in $\text{mm}\cdot\text{s}^{-1}$.

Infrared abbreviations: very strong (vs), strong (s), medium (m), weak (w), shoulder (sh).

RESULTS AND DISCUSSION

Let us consider the infrared data of:

(A):

$\text{vasCOO}^- = (1680\text{s}, 1618\text{vs})$; $\text{vsCOO}^- = (1350\text{w}, 1305\text{s})$; $\delta\text{COO}^- = 800\text{vs}$; $\rho\text{COO}^- = 484\text{w}$; $\omega\text{COO}^- = 415\text{w}$; $\nu\text{MO} = 245\text{m}$; $\nu\text{MX} = 207\text{s}$;

(B):

$\text{vasCOO}^- = 1630\text{s}$; $\text{vsCOO}^- = 1305\text{s}$; $\delta\text{COO}^- = 794\text{m}$; $\rho\text{COO}^- = 480\text{m}$; $\omega\text{COO}^- = 396\text{m}$; $\text{vasSnC}_2 = 288\text{s}$; $\nu\text{MO} = 200\text{sh}$; $\nu\text{MX} = 233\text{m}$;

(C):

$\text{vasCOO}^- = (1631\text{vs}, 1709\text{vs})$; $\text{vsCOO}^- = (1304\text{w}, 1244\text{vw})$; $\delta\text{COO}^- = 794\text{s}$; $\rho\text{COO}^- = 480\text{w}$; $\omega\text{COO}^- = 397\text{m}$; $\text{vasSnC}_2 = 289\text{s}$; $\text{vsSnC}_2 = 261\text{s}$; $\delta\text{asSnC}_2 = 230\text{m}$;

(D):

$\text{vasCOO}^- = (1699\text{vs}, 1630\text{vs})$; $\text{vsCOO}^- = (1348\text{m}, 1305\text{m})$; $\delta\text{COO}^- = 796\text{s}$; $\rho\text{COO}^- = 480\text{s}$; $\omega\text{COO}^- = 388\text{s}$; $\text{vasSnC}_2 = 284\text{s}$; $\nu\text{SnO} = 212\text{s}$; $\nu\text{SnCl} = 252\text{s}$;

(E):

$\text{vasCOO}^- = (1680\text{vs}, 1618\text{vs})$; $\text{vsCOO}^- = (1346\text{w}, 1304\text{s})$; $\delta\text{COO}^- = 802\text{vs}$; $\rho\text{COO}^- = 482\text{m}$; $\omega\text{COO}^- = 409\text{m}$; $\text{vasSnC}_2 = 274\text{vs}$; $\nu\text{SnO} = 212\text{sh}$; $\nu\text{MO} = 242\text{m}$; $\nu\text{MX} = 175\text{m}$;

(F):

$\text{vasCOO}^- = (1680\text{sh}, 1620\text{vs})$; $\text{vsCOO}^- = (1346\text{sh}, 1304\text{s})$; $\delta\text{COO}^- = 796\text{vs}$; $\rho\text{COO}^- = 480\text{s}$; $\omega\text{COO}^- = 397\text{m}$; $\text{vasSnC}_3 = 270\text{s}$; $\nu\text{SnCl}_3 = 255\text{s}$ ($\text{vsSnC}_3 + \nu\text{SnO} + \text{vasSnCl}_3$) = 214vs.

$2(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4) \cdot \text{SnPh}_2\text{C}_2\text{O}_4 \cdot \text{CdC}_2\text{O}_4 \cdot 3\text{CdCl}_2$ (A)

Can be considered as a 1/1 adduct of $\text{SnPh}_2(\text{C}_2\text{O}_4)_2(\text{Me}_4\text{N})_2$ and $\text{Cd}(\text{C}_2\text{O}_4)_2 \cdot 3\text{CdCl}_2$. The first derivative is known as a monohydrate with an octahedrally *cis* coordinated SnPh_2 residue. The suggested structure is reported on Figure 1 with bichelating oxalate anions and chloro bridging metallic centres. The interactions with the cations are of electrostatic type.

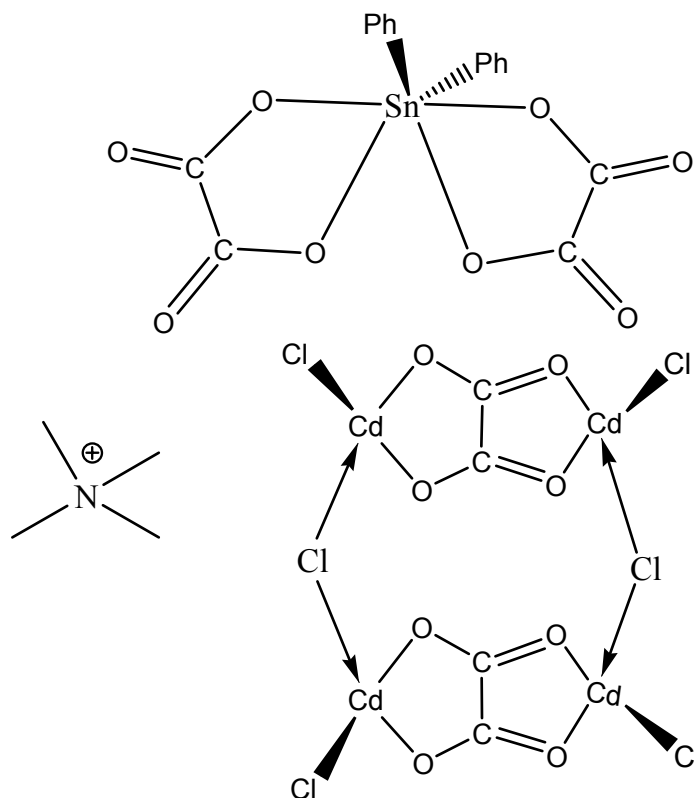


Figure 1. Suggested structure for (A)

$(\text{Me}_4\text{N})_2(\text{C}_2\text{O}_4) \cdot 2\text{SnPh}_2\text{C}_2\text{O}_4 \cdot 2\text{SbCl}_3$ (B)

Can be considered as a central oxalate bichelating two “ SnPh_2^{2+} ” – centres chelated by one $[\text{C}_2\text{O}_4 \cdot \text{SbCl}_3]^-$ complex-anions in left and right sides, leading to the structure reported in Figure 2. It can also be considered as a 1/2 adduct between $(\text{SnPh}_2)_2(\text{C}_2\text{O}_4)_3(\text{Me}_4\text{N})_2$ and SbCl_3 .

$2[(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4] \cdot \text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 2\text{SnPh}_2\text{Cl}_2$ (C)

This adduct can be considered as a 1/1 adduct between $(\text{SnPh}_2)_2(\text{C}_2\text{O}_4)_3(\text{Me}_4\text{N})_2$ and $\text{SnCl}_4\text{C}_2\text{O}_4(\text{Me}_4\text{N})_2$ leading to the structure reported in Figure 3. The interactions with the cations are of electrostatic type.

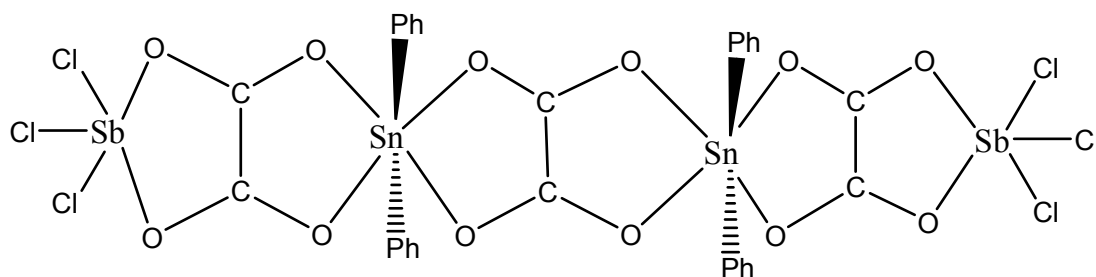


Figure 2. Suggested structure for (B)

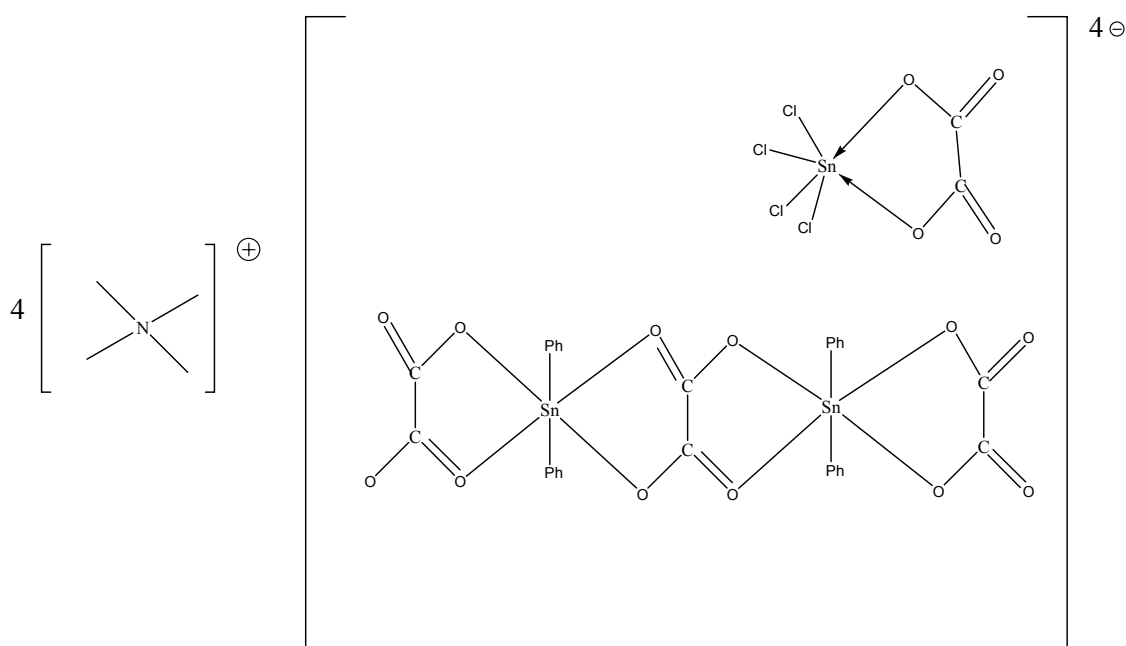


Figure 3. Suggested structure for (C)

(Me₄N)₂(C₂O₄)₂·2Sn(C₂O₄)₂·2SnPh₂Cl₂ (D)

This compound can be considered as a 1/2 adduct between (SnPh₂)₂(C₂O₄)₃(Me₄N)₂ and SnCl₂C₂O₄. This last compound can be considered as a dimer with bridging oxalate anions leading to the structure reported in Figure 4. The interactions with the cations are of electrostatic type.

(Me₄N)₆SnPh₂(C₂O₄)₄·4[SnPh₂(C₂O₄)CdBr₂] (E)

This nonanuclear adduct can be considered as a 2/1 adduct between (SnPh₂)₂(C₂O₄)₃(Me₄N)₂·2CdBr₂ and SnPh₂(C₂O₄)₂(Me₄N)₂; the suggested structure is reported in Figure 5. The interactions with the cations are of electrostatic type.

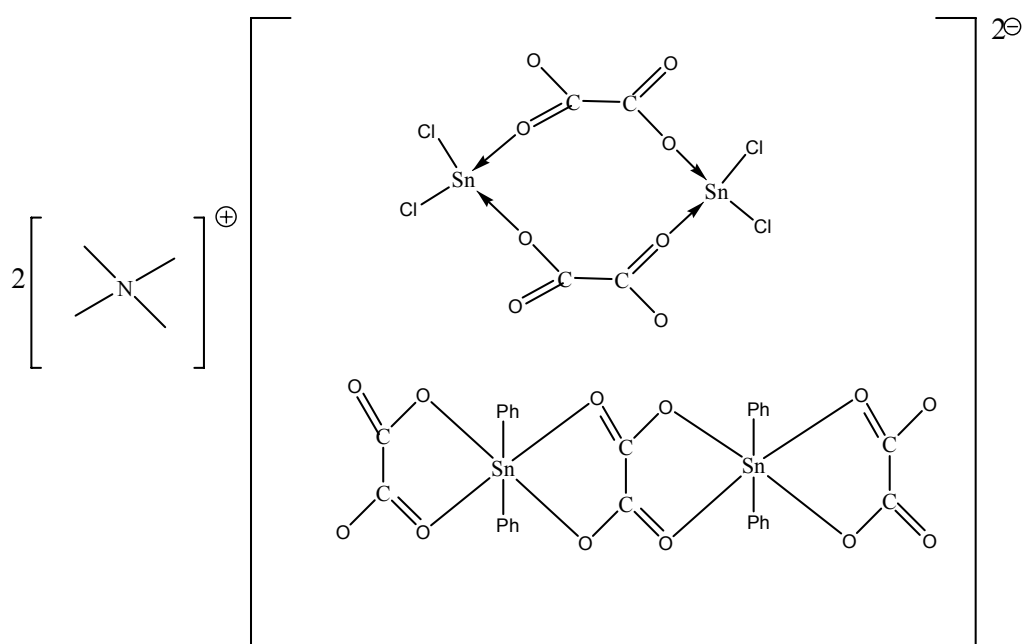


Figure 4. Suggested structure for (D)

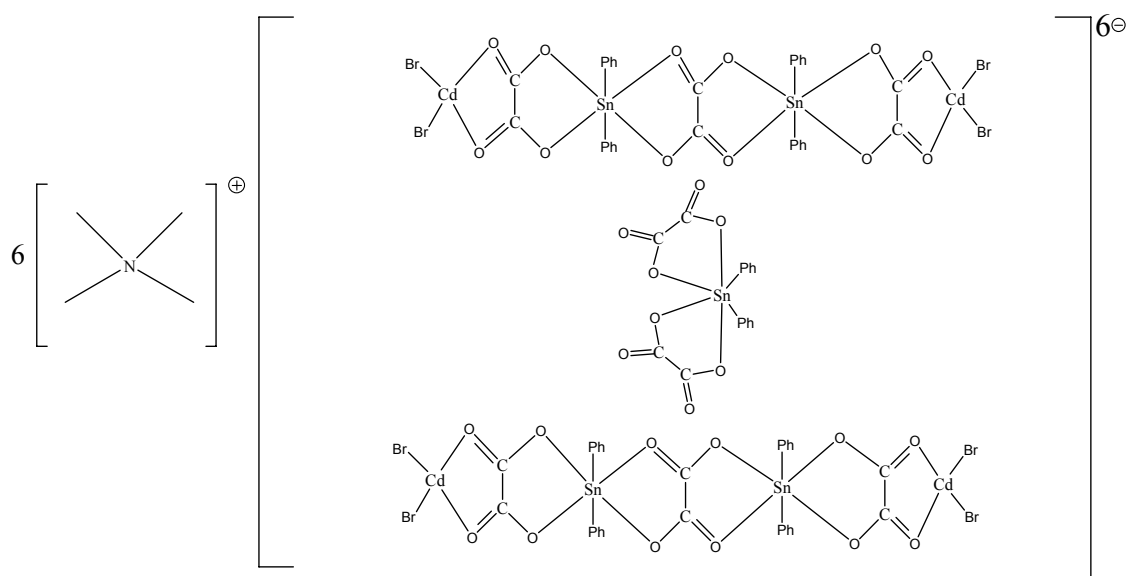


Figure 5. Suggested structure for (E)

$3(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4 \cdot \text{Sn}(\text{C}_2\text{O}_4)_2 \cdot 3\text{SnPh}_2\text{Cl}_2 \cdot 2\text{SnPhCl}_3$ (F)

This compound can be considered as a 1/1/1 adduct between $(\text{SnPh}_2)_2(\text{C}_2\text{O}_4)_3(\text{Me}_4\text{N})_2$, $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4(\text{SnPh}_2\text{Cl}_2)_2$ and $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4(\text{SnCl}_4)_2$ (Figure 6).

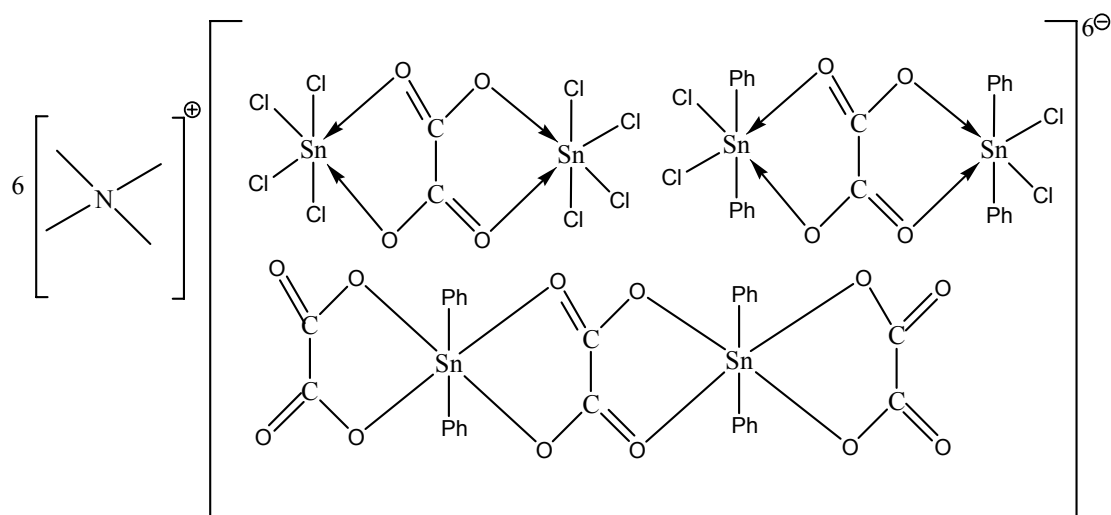


Figure 6. Suggested structure for (F)

The dinuclear adducts $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4(\text{SnPh}_2\text{Cl}_2)_2$ and $(\text{Me}_4\text{N})_2\text{C}_2\text{O}_4(\text{SnCl}_4)_2$ present in this structure have already been reported by us in [12 – 24].

CONCLUSION

Mainly the adducts studied have discrete structure and are insertion adducts containing in many cases $[(\text{SnPh}_2)_2(\text{C}_2\text{O}_4)_3]^{2-}$ in interactions with $[\text{C}_2\text{O}_4.\text{SnCl}_4]^{2-}$, $[\text{C}_2\text{O}_4(\text{SnCl}_4)_2]^{2-}$ or $[\text{C}_2\text{O}_4(\text{SnPh}_2\text{Cl}_2)_2]^{2-}$ complex anion, the oxalate behaving in all cases at least as a monochelating ligand, in many cases as a bichelating one. The antimony containing adduct is a classical one in terms of Lewis acid and base interactions.

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