

NEW CHROMATO DERIVATIVES AND ADDUCTS: SYNTHESIS, INFRARED AND MÖSSBAUER STUDIES

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Received: July 13, 2010

Accepted: December 15, 2010

Abstract: Eight new chromato organostannic adducts have been synthesized and studied by infrared and Mössbauer spectroscopy. Discrete, polymeric and supramolecular structures have been suggested, the environment around the tin centre being in all cases, trigonal bipyramidal.

Keywords: *chromato, discrete, infrared, Mössbauer, polymeric, residue, SnR₃ (R = Ph, Me), supramolecular structures.*

INTRODUCTION

The discovery of the biological activity of $\text{SnPh}_3\text{O}_2\text{CPh}$ against some types of cancer [1] explains the research activity until nowadays on SnR_3 ($\text{R} = \text{Me}, \text{Bu}, \text{Ph}$) residues containing organotin (IV) compounds [2 – 6]. Very few X ray structures of organotin (IV) chromato compounds have been determined [7 – 9]. In our research work dealing with the coordinating ability of the oxyanions in organotin (IV) chemistry, we have yet reported some papers including spectroscopic work and X ray structure determination of chromato derivatives [7 – 10]. In the framework of our research work seeking new organotin (IV) compounds, we report here the synthesis and the spectroscopic characterization of some new chromato derivatives and adducts. Structures are suggested on the basis of the spectroscopic data.

EXPERIMENTAL

On allowing CrO_3 in water to react with SnPh_3OH in ethanol, a yellow powder is obtained after a slow solvent evaporation; its analytical data: % calculated (% found): $\text{C} = 44.57$ (44.28); $\text{H} = 3.74$ (3.42); allow to conclude to **$\text{HCrO}_4\text{SnPh}_3 \cdot \text{H}_2\text{O}$ (A)** as formula.

When $\text{HCrO}_4\text{SnPh}_3 \cdot \text{H}_2\text{O}$ in MeOH is mixed with Cy_2NH in water, a yellow powder is obtained after a slow solvent evaporation. Its analytical data: % calculated (% found): $\text{C} = 55.58$ (55.52); $\text{H} = 6.06$ (6.11); $\text{N} = 2.16$ (2.08); allow to conclude to the presence of **$\text{Cy}_2\text{NH}_2\text{CrO}_4\text{SnPh}_3$ (B)**.

When $\text{Cy}_2\text{NH}_2\text{HCrO}_4 \cdot 2\text{H}_2\text{O}$ - obtained on mixing CrO_3 in water with Cy_2NH in 1/1 ratio - is mixed with SnMe_3Cl in chloroform in 1: 1 ratio, a yellow powder is obtained after a slow solvent evaporation. Its analytical data: % calculated (% found): $\text{C} = 38.98$ (38.21); $\text{H} = 7.20$ (7.10); $\text{N} = 3.03$ (3.10); allow to conclude to **$\text{Cy}_2\text{NH}_2\text{CrO}_4\text{SnMe}_3$ (C)** as formula.

The same reaction in MeOH gives a yellow powder after a slow solvent evaporation. Its analytical data: % calculated (% found): $\text{C} = 52.77$ (51.96); $\text{H} = 8.06$ (8.11); $\text{N} = 4.73$ (4.75); allow to suggest **$(\text{Cy}_2\text{NH}_2)_2\text{CrO}_4 \cdot \text{SnMe}_3\text{Cl} \cdot \text{Cy}_2\text{NH}_2\text{Cl}$ (D)** as formula.

When $\text{HCrO}_4\text{SnPh}_3 \cdot \text{H}_2\text{O}$ in MeOH is mixed with Hexyl Ph_3PBr in ethanol a yellow powder is obtained after a slow solvent evaporation. The analytical data of this compound: % calculated (% found): $\text{C} = 60.39$ (60.50); $\text{H} = 5.19$ (5.15) allow to conclude to the presence of **$(\text{PPh}_3\text{Hexyl})_2\text{CrO}_4 \cdot 2\text{SnPh}_3\text{Br}$ (E)**.

On allowing 1-phenyl, 2,3 butadione to react with $\text{SnPh}_3\text{CrO}_4\text{H}$ in ethanol in 1 : 1 ratio, a yellow powder is obtained after a slow solvent evaporation. Its analytical data: % calculated (% found): $\text{C} = 53.02$ (5.26); $\text{H} = 4.93$ (4.84); allow to suggest **$\text{PhCOCH}_2\text{COCH}_3\text{SnPh}_3\text{CrO}_4\text{H}$ (F)** as formula.

On allowing 1-phenyl, 2,3 butadione to react with $\text{SnPh}_3\text{CrO}_4\text{H}$ in ethanol in 1 : 2 ratio, a yellow powder is obtained after a slow solvent evaporation. The analytical data of this compound: % calculated (% found): $\text{C} = 51.76$ (51.72); $\text{H} = 4.73$ (4.44) allow to suggest **$(\text{PhCOCH}_2\text{COCH}_3)_3(\text{SnPh}_3\text{CrO}_4\text{H})_2$ (G)** as formula.

On allowing $\text{SnPh}_3\text{CrO}_4\text{H}$ in ethanol to react with OPPh_3 in ethanol in 1 : 1 ratio, a yellow powder is obtained after slow solvent evaporation. Its analytical data:

% calculated (% found): C = 53.50 (53.55); H = 4.91 (4.03) allow to conclude to **(SnPh₃CrO₄H)₂OPPh₃ (H)** as formula.

The elemental analyses were performed by the CNRS "Service Central d'Analyses" Vernaison (France), the Faculty of Chemistry University of Konstanz (Germany) and the Microanalytical Centre, University of Bath (UK). The infrared spectra were recorded at the University of Cheikh Anta Diop, Dakar (Senegal) and the University of Padova (Italy), using a PE 580 (4000 – 200 cm⁻¹) or a Bruker FTIR spectrometer, the sample being as Nujol mulls, the windows being CsI or polyethylene. Mössbauer spectra were obtained as described previously [11]. Infrared data are given in cm⁻¹ [abbreviations: (vs) very strong, (s) strong, (m) medium, (sh) shoulder, (w) weak, (vw) very weak]. Mössbauer parameters are given in mm·s⁻¹ (abbreviations: Q.S. = quadrupole splitting, I.S. = isomer shift, Γ = full width at half-height).

All the chemicals were from Aldrich or Merck companies and used without any further purification.

RESULTS AND DISCUSSION

Let us consider the IR data of these derivatives and adducts:

- (A): (ν_1 and ν_3) CrO₄²⁻ = 856 vs, 880 m, ν_{as} SnC₃ = 271 vs, δ_{as} SnC₃ = 238 s, ν SnO = 219 s, ν_s SnC₃ = 212 sh, δ_s SnC₃ = 160 s;
 (B): (ν_1 and ν_3) CrO₄²⁻ = 816 vs, 888 vs, ν_{as} SnC₃ = 274s, δ_{as} SnC₃ = 238 s, ν SnO = 228 sh, δ_s SnC₃ = 160 s;
 (C): (ν_1 and ν_3) Cr O₄²⁻ = 820 vs, 888 vs, ν_{as} SnC₃ = 546 s;
 (D): (ν_1 and ν_3) Cr O₄²⁻ = 816 vs, 866 vs, ν_{as} SnC₃ = 550 s, ν_s SnC₃ = 520 vw;
 (E): (ν_1 and ν_3) Cr O₄²⁻ = 810 vs, 830 vs, ν_{as} SnC₃ = 267 s, δ_{as} SnC₃ = 239 m, ν SnO = 221sh, ν_s SnC₃ = 210 vw, δ_s SnC₃ = 160 m;
 (F): (ν_1 and ν_3) CrO₄²⁻ = 860 vs, ν_{as} SnC₃ = 267 s, δ_{as} SnC₃ = 239 s, ν SnO = 239 m, ν_s SnC₃ = 213 sh, δ_s SnC₃ = 160 m;
 (G): (ν_1 and ν_3) CrO₄²⁻ = 865 vs, ν_{as} SnC₃ = 268 vs, δ_{as} SnC₃ = 237 s, ν SnO = 210 s, ν_s SnC₃ = 220 vw, δ_s SnC₃ = 157 m;
 (H): (ν_1 and ν_3) CrO₄²⁻ = 798 vs, 859 m, ν_{as} SnC₃ = 277 vs, δ_{as} SnC₃ = 239 s, ν SnO = 228 s, ν_s SnC₃ = 215 vw, δ_s SnC₃ = 175s;

and their Mössbauer data:

- (A): Q.S. = 3.12 mm·s⁻¹, I.S. = 1.40 mm·s⁻¹;
 (B): Q.S. = 2.91 mm·s⁻¹, I.S. = 1.21 mm·s⁻¹;
 (D): Q.S. = 3.00 mm·s⁻¹, I.S. = 1.23 mm·s⁻¹.

HCrO₄SnPh₃·H₂O (A)

The value of the quadrupole splitting - 3.12 mm·s⁻¹ - indicates the presence of a transcoordinated SnPh₃ residue according to Platt *et al.* [12, 13] and allows to suggest a polymeric structure with a trigonal bipyramidal environment around the tin (IV) centre; the presence of OH----O hydrogen bonds responsible of the wide absorption around 2900 cm⁻¹ on the IR spectrum allows to consider secondary interactions leading to a supramolecular architecture (Figure 1).

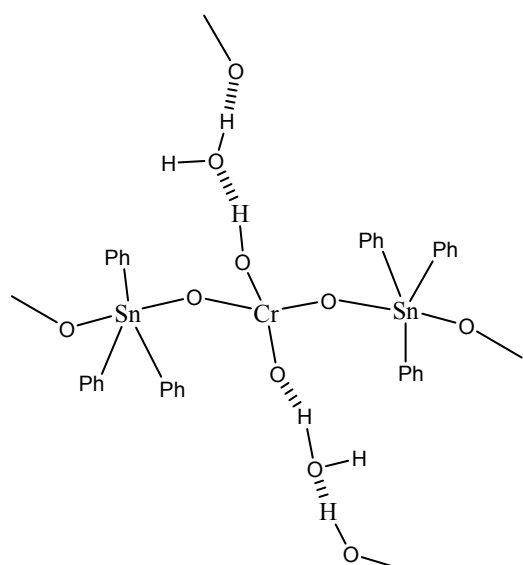


Figure 1. Structure of derivative
A - $\text{HCrO}_4\text{SnPh}_3 \cdot \text{H}_2\text{O}$

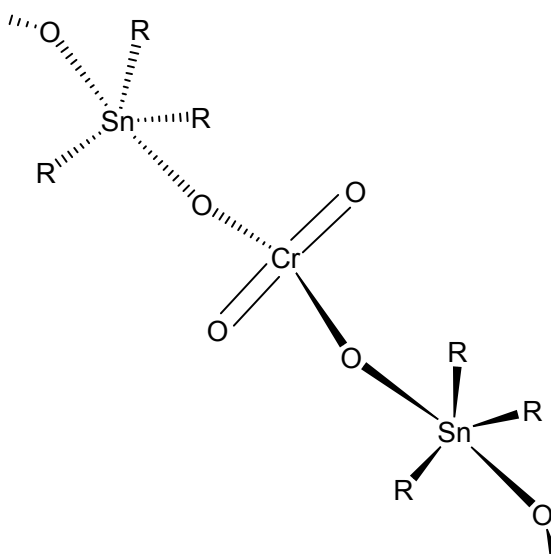


Figure 2. Structure of derivatives
B and **C** - $\text{Cy}_2\text{NH}_2\text{CrO}_4\text{SnR}_3$ ($\text{R} = \text{Ph}, \text{Me}$)

$\text{Cy}_2\text{NH}_2\text{CrO}_4\text{SnR}_3$ ($\text{R} = \text{Ph}, \text{Me}$) (**B**), (**C**)

The quadrupole splitting of (**B**) - $2.91\text{mm}\cdot\text{s}^{-1}$ - and the absence of the ν_{SnC_3} in the IR spectrum of (**C**) allow to conclude to the presence of a transcoordinated SnR_3 residue according to Platt *et al.* [12, 13] for (**B**) and Nakamoto [14] for (**C**) and allow to suggest an infinite chain structure similar to the one reported for $\text{Bu}_4\text{NWO}_4\text{SnMe}_3$ and $\text{Bu}_4\text{NMoO}_4\text{SnMe}_3$ by Rosenland *et al.* [15] (Figure 2) - the similarity of the formulae of the compounds in [15] with (**B**) and (**C**) is noteworthy.

$(\text{Cy}_2\text{NH}_2)_2\text{CrO}_4 \cdot \text{SnMe}_3\text{Cl} \cdot \text{Cy}_2\text{NH}_2\text{Cl}$ (**D**)

The appearance of ν_{SnC_3} as a very weak band allows concluding to the presence of a planar SnMe_3 residue [14]. We can consider SnMe_3Cl linked to Cl^- and giving $[\text{SnMe}_3\text{Cl}_2]^-$ or SnMe_3Cl directly linked to the oxyanion. So, two structures are suggested (Figures 3a, 3b).

In the first structure which is dimeric, the complex-ions $[\text{SnMe}_3\text{Cl}_2]^-$ are linked to the anion through the cation by means of $\text{NH} \cdots \text{Cl}$ hydrogen bonds.

The second suggested structure is a tetranuclear one with O coordinated SnMe_3Cl . The two monomers are connected by $\text{Cy}_2\text{NH}_2^+ \cdots \text{Cl} \cdots \text{Cy}_2\text{NH}_2^+$ strings, this dimer leads to a dimer of dimer when the remaining cations are involved through $\text{NH} \cdots \text{O}$ hydrogen bonds.

While comparing compounds (**C**) and (**D**) we can outline that the less polar solvent (chloroform) has allowed the elimination of one molecule of $\text{Cy}_2\text{NH}_2\text{Cl}$ while the polar one (MeOH) does not allow it. The reaction equations are:



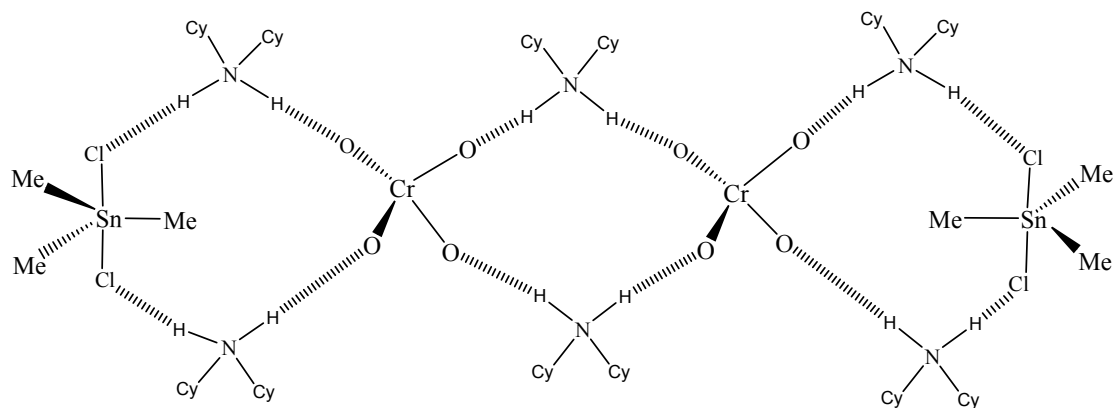
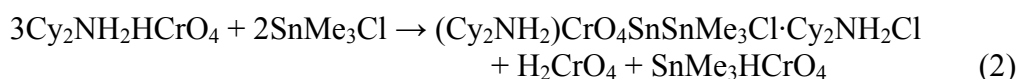


Figure 3a. Dimeric structure of the complex **D** - $(\text{Cy}_2\text{NH}_2)_2\text{CrO}_4\cdot\text{SnMe}_3\text{Cl}\cdot\text{Cy}_2\text{NH}_2\text{Cl}$

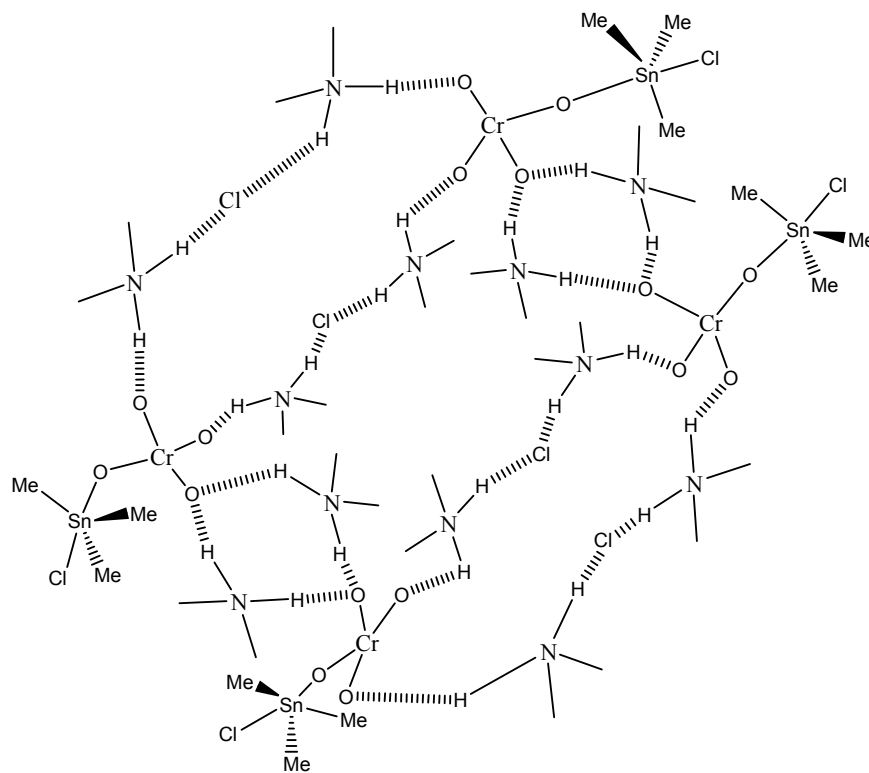


Figure 3b. Structure of complex **D** - $(\text{Cy}_2\text{NH}_2)_2\text{CrO}_4\cdot\text{SnMe}_3\text{Cl}\cdot\text{Cy}_2\text{NH}_2\text{Cl}$

(PPh₃Hexyl)₂CrO₄·2SnPh₃Br (E)

For this compound the quadrupole splitting value - Q.S. = 3.00 mm·s⁻¹ - allows to suggest the presence of a coordinated SnPh₃Br according to Platt *et al.* [12, 13] in comparison with the Q.S. value of free SnPh₃Br (2.50 mm·s⁻¹) [12, 13] and allow to

suggest a trigonal bipyramidal environment around the tin (IV) centre. A discrete structure with bidentate CrO_4^{2-} oxyanion is suggested (Figure 4).

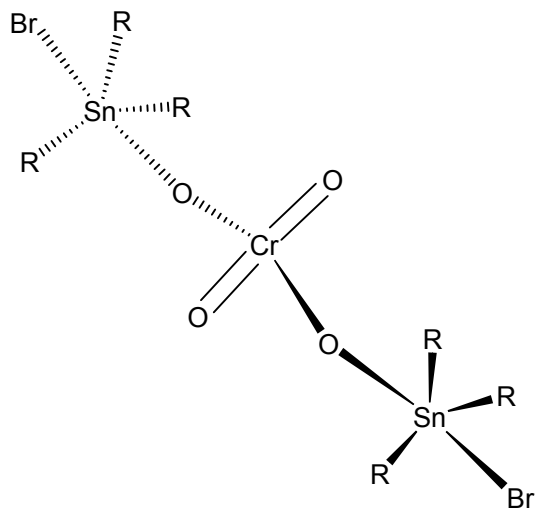


Figure 4. Discrete structure of complex **E** - anion $\text{CrO}_4^{2-}2\text{SnPh}_3\text{Br}^{2-}$

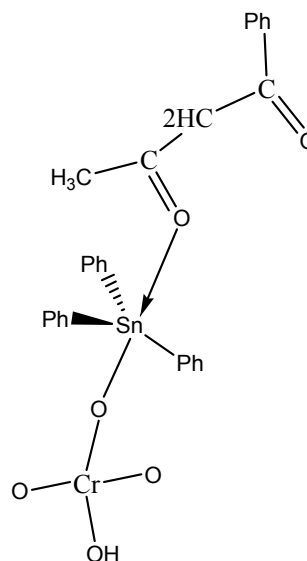


Figure 5. Discrete structure of complex **F** - $\text{PhCOCH}_2\text{COCH}_3\text{SnPh}_3\text{CrO}_4\text{H}$

$\text{PhCOCH}_2\text{COCH}_3\text{SnPh}_3\text{CrO}_4\text{H}$ (F),
 $(\text{PhCOCH}_2\text{COCH}_3)_3(\text{SnPh}_3\text{CrO}_4\text{H})_2$ (G),
 $(\text{SnPh}_3\text{CrO}_4\text{H})_2\text{OPPh}_3$ (H)

In the absence of Mössbauer data, we can consider that the appearance of ν_{SnC_3} as a weak band around 215 cm^{-1} on the IR spectrum of **(F)** - **(H)** is an indication of the presence of a nearly planar SnPh_3 residue [14] allowing to suggest, for the three compounds, the presence of a trigonal bipyramidal environment around the tin (IV) centre.

We suggest therefore for **(F)** a discrete structure with a monodentate hydrogenochromate (Figure 5).

In the case of **(G)** a discrete structure is suggested with two $\text{CrO}_4\text{HSnPh}_3 \cdot \text{PhCOCH}_2\text{COCH}_3$ molecules linked by one $\text{PhCOCH}_2\text{COCH}_3$ molecule via $\text{OH} \cdots \text{O}$ hydrogen bonds (Figure 6).

The suggested structure for **(H)** is discrete with two $\text{CrO}_4\text{HSnPh}_3$ molecules linked via the oxygen atom of OPPh_3 ligand (Figure 7).

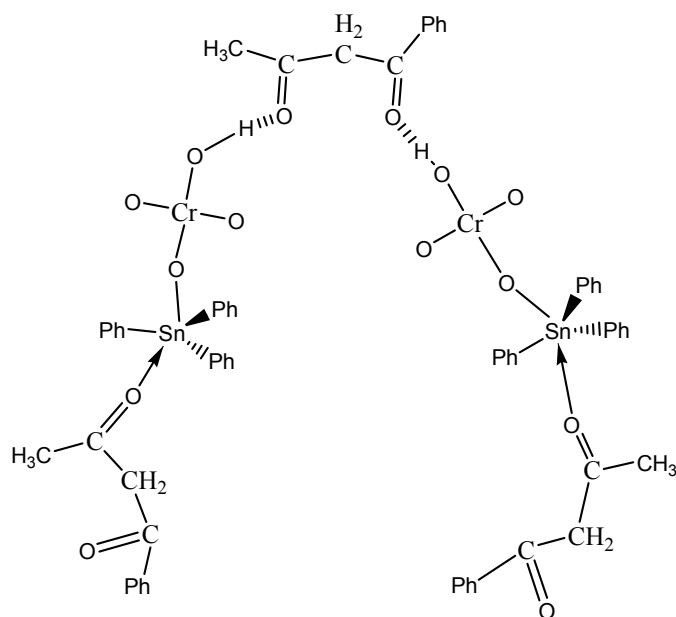


Figure 6. Discrete structure of complex **G**

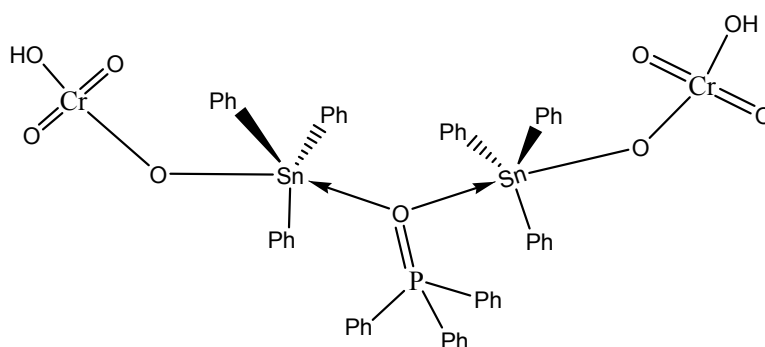


Figure 7. Discrete structure of complex **H**

CONCLUSION

The chromato derivatives studied have infinite chain type structures, the anion behaving as a polydentate ligand (supramolecular structures are present when the cation is involved). The SnPh_3 residue is in all cases *trans* coordinated.

ACKNOWLEDGEMENTS

The Dakar group thanks Professor M. Vidali for equipment support and performing part of the elemental analyses.

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