

Syntheses, Mössbauer and Infrared Spectroscopic Investigations on Tin(II) Chloride Adducts with Purine and Pyrimidine Bases and Nucleosides

L. PELLERITO, G. RUISI, M. T. LO GIUDICE,

Gruppo di Chimica dei Composti Organometallici, Università di Palermo, 90123 Palermo, Italy

J. D. DONALDSON and S. M. GRIMES

Department of Chemistry, The City University, Northampton Square, London EC1V 0HB, U.K.

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The synthesis of two types of tin(II) complex $\text{SnCl}_2 \cdot \text{L} \cdot \text{CH}_3\text{OH}$ ($\text{L} = \text{adenosine, cytidine and inosine}$) and $\text{SnCl}_2 \cdot \text{L}_2 \cdot \text{CH}_3\text{OH}$ ($\text{L} = \text{adenine and cytosine}$) are described. The complexes are characterised by their infrared and ^{119}Sn Mössbauer data. The Mössbauer shift data suggest that the bonds between tin(II) chloride and the donor atoms of the ligands are relatively weak.

Introduction

Tin(II) chloride is known to form adducts with a wide variety of oxygen- and nitrogen-donor molecules [1–6] but there have been few reports of complex formation with purine and pyrimidine bases or nucleosides. Tin-119 Mössbauer parameters and thermal decomposition data for the tin(II) chloride

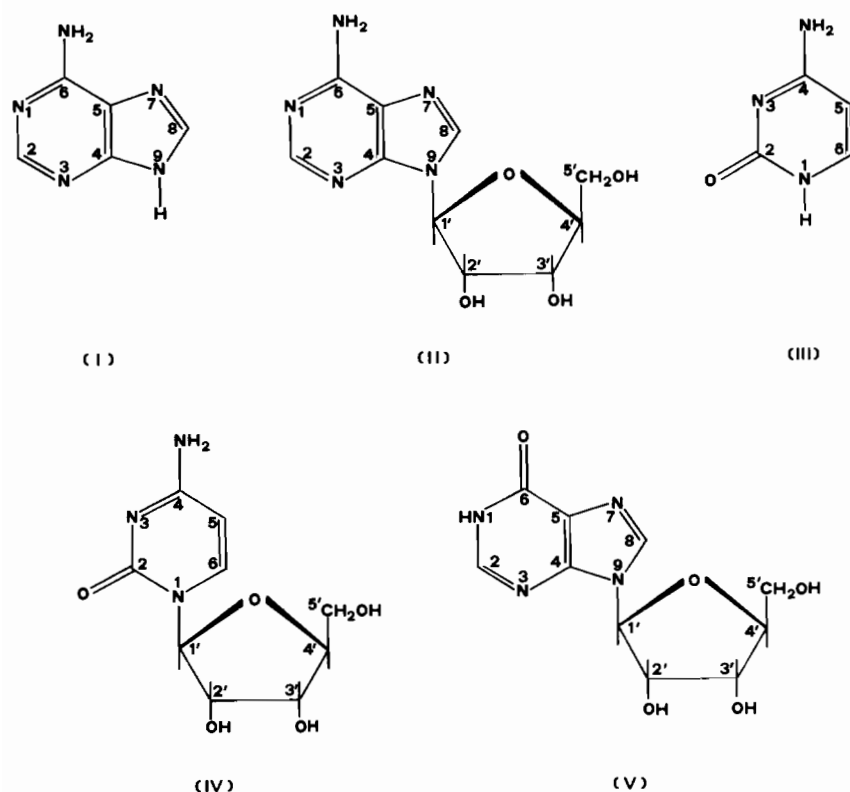


Fig. 1. I–V. The donor molecules under study.

TABLE I. Analytical Data for the Complexes $\text{SnCl}_2 \cdot \text{L}_n \cdot \text{CH}_3\text{OH}$ (theoretical values in parentheses).

$\text{SnCl}_2 \cdot \text{L}_n \cdot \text{CH}_3\text{OH}$ $\text{L}^a =$	n =	Sn %	Cl %	C %	H %	N %	CH_3OH %
Adenine	2	23.7 (24.13)	13.7 (14.40)	26.9 (26.85)	2.7 (2.86)	28.9 (28.47)	7.0 (6.5)
Cytosine	2	26.3 (26.74)	16.1 (15.98)	24.9 (24.35)	2.8 (3.18)	18.8 (18.93)	8.0 (7.2)
Adenosine	1	25.1 (24.28)	14.4 (14.50)	26.8 (27.02)	3.3 (3.05)	14.4 (14.32)	6.0 (6.5)
Cytidine	1	25.6 (25.53)	16.1 (15.25)	26.2 (25.83)	3.4 (3.68)	9.6 (9.04)	8.0 (6.9)
Inosine	1	24.1 (24.23)	15.0 (14.47)	27.5 (26.97)	3.1 (3.29)	11.6 (11.43)	6.5 (6.5)

^a Adenine = 6-aminopurine; cytosine = 4-amino-2-hydroxypyrimidine; Adenosine = Adenine-9- β -D-ribofuranoside; Cytidine = cytosine-1- β -D-ribofuranoside; Inosine = Hypoxanthine-9- β -D-ribofuranoside.

complexes with monodentate oxygen- or nitrogen-donor molecules are consistent with the expected predominant monofunctional acceptor properties of tin(II) chloride to give the preferred trigonal pyramidal coordination of tin(II). Any additional ligands in the complexes are either only weakly bonded or not bonded to tin. In many cases, for example $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, where only one water molecule is directly bonded to the tin [7], the additional ligands appear to be present only for lattice packing purposes. Relatively few tin(II) complexes of tin(II) chloride with multidentate ligands have been studied. In tin(II) chloride-1,4-dioxan the ligand molecules bridge the SnCl groups to form two relatively long Sn-O bonds to each tin atom, resulting in a distorted four pyramidal environment for tin(II) [8]. There is no evidence [6] in the infrared spectra of $\text{SnCl}_2 \cdot 2$ -morpholine for the formation of the Sn-O bonds and it appears that only the nitrogen atoms of this ligand are acting as donors. In this work we describe the adducts formed between tin(II) chloride and purine and pyrimidine bases or nucleosides that could act as multidentate ligands. The donor molecules studied are adenine, adenosine, cytosine, cytidine and inosine (Fig. 1, I-V). Two types of complex are identified, $\text{SnCl}_2 \cdot \text{L} \cdot \text{CH}_3\text{OH}$ (L = adenosine, cytidine and inosine) and $\text{SnCl}_2 \cdot \text{L}_2 \cdot \text{CH}_3\text{OH}$ (L = adenine and cytosine) and are characterized by chemical analysis and by their infrared and ¹¹⁹Sn Mössbauer data.

Experimental

Preparation of the Complexes

All of the complexes described in this work were prepared by refluxing a solution containing SnCl_2 in dry methanol with the appropriate molar proportions of the ligands under an atmosphere of oxygen-

free nitrogen for 3-10 hours. The products were filtered under nitrogen, washed with dry methanol and dried under vacuum.

Analysis of the Complexes

Tin analyses of the products were carried out both by a tin(IV) oxide gravimetric procedure and Donaldson and Moser's method [9]. Chlorine was determined both by potentiometric titration and by titration with mercuric perchlorate following the destruction of organic matter by the oxygen flask method. C, H and N contents were determined at the Istituto di Chimica Organica (Milano). The methanol solvation of the complexes was determined by thermogravimetric analysis using a Stanton Redcroft 750 Thermobalance. The analytical data are in Table I.

Results and Discussion

Infrared Data for Complexes

Table II contains the more important infrared frequencies for the tin(II) chloride complexes. Small changes are observed in the νNH_2 vibrations and in the vibrations of the purine and pyrimidine rings for all of the complexes in comparison with the data for the free ligands. These changes appear to occur as a result of inductive effects in the systems irrespective of the site of co-ordination to the tin [10]. The most significant change observed in the adenine complex in comparison to the free ligand species is the loss of $\delta\text{N-H}$ frequency associated with the atom N(9) of the free ligand [$870(\text{m}) \text{ cm}^{-1}$] [11]. This suggests that the co-ordination of adenine to tin(II) chloride occurs at N(9), which is the usual co-ordination site for unblocked adenine type ligands to metal moieties [12]. The spectra of the adenine complex also con-

TABLE II. Relevant Infrared Data for Tin(II) Chloride Adducts.^a

Compound ^b	νNH_2	$\nu\text{C=O}$	δNH_2	$\delta\text{(N(1)-H)}$ in plane	$\delta\text{(N(1)-H)}$ out of plane	$\nu\text{C-O}$ in C-OH Sn	$\nu\text{Sn-Cl}$
$\text{SnCl}_2(\text{Ade})_2 \cdot \text{MeOH}$	3320 w 3160 w		1672 s				280 w
$\text{SnCl}_2(\text{Cyt})_2 \cdot \text{MeOH}$	3340 m 3180 m	1722 s	1677 m	1538 m	823 m		330 w
$\text{SnCl}_2\text{Ado} \cdot \text{MeOH}$	3320 m 3140 m 3100 w		1685 m			1092 s,bd	320 w
$\text{SnCl}_2\text{Cyd} \cdot \text{MeOH}$	3340 s 3180 m	1625 s	1670 s			1090 s,bd	320 w
$\text{SnCl}_2\text{Ino} \cdot \text{MeOH}$	3330 m 3190 m	1690 s,bd		1538 w	823 m	1080 s,bd	320 w

^aIn the 4000–250 cm^{-1} region; measured in Nujol and hexachlorobutadiene mulls with a Perkin-Elmer mod. 580 spectrometer; s = strong, m = medium, w = weak, bd = broad. ^bAde = Adenine; Cyt = Cytosine; Ado = Adenosine; Cyd = Cytidine; Ino = Inosine.

TABLE III. Mössbauer Parameters at Liquid N_2 Temperature.

Compound	$\delta\text{ mm s}^{-1}$ ^a	$\Delta\text{ mm s}^{-1}$ ^b	Ref.
1. $\text{SnCl}_2(\text{Ade})_2\text{MeOH}$	3.40	1.60	This work
2. $\text{SnCl}_2(\text{Cyt})_2 \cdot \text{MeOH}$	3.43	1.45	This work
3. $\text{SnCl}_2 \cdot \text{Ado} \cdot \text{MeOH}$	3.50	1.54	This work
4. $\text{SnCl}_2 \cdot \text{Cyd} \cdot \text{MeOH}$	3.39	1.57	This work
5. $\text{SnCl}_2 \cdot \text{Ino} \cdot \text{MeOH}$	3.55	1.54	This work
6. SnCl_2	4.12	0	4
7. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	3.68	1.21	4
8. $\text{SnCl}_2 \cdot 2\text{Me}_2\text{SO}$	3.48	1.39	4
9. $\text{SnCl}_2 \cdot 1,4\text{-Dioxan}$	3.76	1.61	4
10. $\text{SnCl}_2 \cdot \text{py}$	3.29	0.98	2
11. $\text{SnCl}_2 \cdot \text{piperazine}$	2.87	2.17	5
12. $\text{SnCl}_2 \cdot 2\text{morpholine}$	2.81	2.24	5
13. $\text{SnCl}_2 \cdot 2\text{piperidine}$	2.81	2.21	5

^aIsomer shift with respect to R.T. CaSnO_3 . ^bNuclear quadrupole splitting.

tain a band at 280 cm^{-1} , assignable to the SnCl vibration. The ligand cytosine usually forms complexes to metal species at the heterocyclic N(3) atom. Coordination at this site results in formation of strong bands in the C=O stretching region of the spectrum [12]. The appearance of the band at 1722 cm^{-1} in the $\text{SnCl}_2(\text{cytosine})_2\text{MeOH}$ complex, and the fact that the $\delta_{\text{N-H}}$ in plane and out of plane frequencies associated with N(1) are not changed in going from the ligand to the complex, is consistent with co-ordination at N(3). The value of $\nu(\text{C=O})$ of 1722 cm^{-1} is higher than the value in the free ligand in contrast to the lower values found in other metal

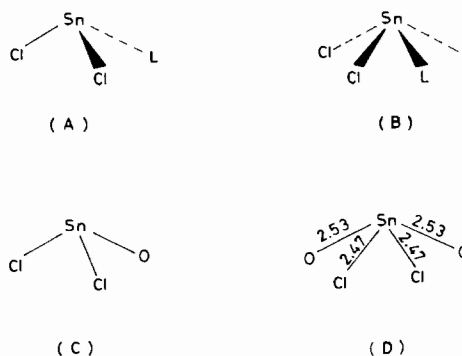
complexes of the type $\text{M}(\text{cytosine})_2\text{X}_2$ [12] compounds which all have $\nu(\text{C=O})$ values lower than 1703 cm^{-1} in cytosine. Values of $\nu(\text{C=O})$ higher than the cytosine value are however found in hydrated $\text{M}(\text{cytosine})_2\text{X}_2$ compounds and interpreted in terms of hydrogen bonding of cytosine to solvate molecules which in turn are coordinated to the metal ion [12]. It is possible that the band at 1722 cm^{-1} arises because of the presence of solvated methanol but it is unlikely that the methanol could be co-ordinated to the tin. The band at 330 cm^{-1} in the cytosine complex is assigned to $\nu\text{Sn-Cl}$. The adenosine ligand can be regarded as an adenine molecule with the

favoured N(9) donor atom position blocked, so that co-ordination must occur either through other nitrogen atoms of the nucleoside or through oxygen atoms of the carbohydrate groups. The only major changes in the spectra of the adenosine complex in comparison with the free ligand are in the C—O stretching region of the carbohydrate group. The changes in the spectra of the heterocyclic ring system on complex formation are typical of those found when bonding to a metal occurs at any atom in the molecule, including at the carbohydrate oxygen atoms [14]. The infrared data therefore suggest that at least one of the carbohydrate hydroxyl groups is bonded to the tin. The data do not however exclude the possibility of either donation by both oxygens in the carbohydrate hydroxyl groups or of donation from one of these oxygen atoms and of N(7) from the pyrimidine ring. The band at 320 cm^{-1} in the adenosine complex is assigned to $\nu\text{Sn—Cl}$. The major changes in the spectra of the tin(II) chloride complexes with cytidine and inosine are also in the νCO stretching region of the carbohydrate group and the bonding to tin is presumably similar to that in the adenosine complex. Bands in the cytidine and inosine complexes at 320 cm^{-1} are again assigned to Sn—Cl vibrations.

^{119}Sn Mössbauer Spectra for the SnCl_2 Complexes

The Mössbauer parameters were obtained by published methods [15] and the data are in Table III, along with the parameters for related compounds. The chemical isomer shifts for the new complexes 1–5 lie in the narrow range $3.40\text{--}3.55\text{ mm s}^{-1}$. These shifts are lower than that for SnCl_2 and this is consistent with complex formation involving the replacement of a bridging anion in the trigonal pyramidal coordination of tin(II) chloride with stronger tin(II) to donor atom bonds. The i.r. data for the complexes $\text{SnCl}_2 \cdot \text{L} \cdot \text{CH}_3\text{OH}$ 3–5 show that the tin atoms are bonded to oxygen atoms of the carbohydrate groups in the ligands. The data for the $\text{SnCl}_2 \cdot \text{L}_2 \cdot \text{CH}_3\text{OH}$ complexes 1 and 2, however, show that the tin is bonded to ligand N-atoms. Two main types of tin(II) chloride adduct are possible, *viz.* (1) the formation of a trigonal pyramidal tin(II) moiety (A) by coordination to only one donor atom of the ligand or (2) the formation of a distorted four pyramidal moiety (B) by coordination to two donor atoms of the ligand. These types of complex are illustrated by the tin(II) environments in $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (C) and $\text{SnCl}_2 \cdot 1,4\text{-dioxan}$ (D).

The Mössbauer chemical isomer shift gives some indication of the strength of the complexes formed with tin(II) chloride in that lower shift values indicate the presence of stronger covalent bonds. The typical length of a Sn—O bond is 2.14 \AA [16] and so the SnO distance in C represents a relatively weak donor–acceptor interaction. The presence of two



even weaker Sn—O interactions (2.53 \AA) in D is reflected in the small difference (0.39 mm s^{-1}) in shift between SnCl_2 and $\text{SnCl}_2 \cdot 1,4\text{-dioxan}$ but these bonds are very long. In the $\text{SnCl}_2 \cdot \text{nucleoside}$ complexes Sn can be bonded either to one oxygen or to two oxygen atoms of the carbohydrate group to give either a three or a four-coordinated tin environment. The bonds formed however must be somewhat shorter than those found in $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{SnCl}_2 \cdot 1,4\text{-dioxan}$ respectively. The chemical isomer shifts for the adenine and cytosine complexes are higher than those found in typical SnCl_2 adducts with nitrogen-donor molecules suggesting that the Sn—N interactions in compounds 1 and 2 are again relatively weak. The Mössbauer quadrupole couplings for compounds 1–5 are in the range $1.45\text{--}1.60\text{ mm s}^{-1}$ and would be consistent with low symmetry tin environments containing a lone-pair of electrons and a weak tin–ligand interaction.

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