

**SYNTHESIS, I. R. AND MÖSSBAUER STUDIES OF SELENITO
AND PHENYLARSENATO SnCl_4 AND MX_2 ADDUCTS
($\text{M} = \text{Cd}, \text{Hg}$; $\text{X} = \text{Cl}, \text{Br}$)**

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Résumé : Neuf complexes des anions sélénite et phénylarséniate ont été synthétisés et caractérisés par spectroscopie infrarouge et Mössbauer. Les oxoanions se comportent comme polychélatants, polydentates ou tridentates pontants donnant ainsi des structures discrètes ou polymères.

Mots clés : Complexes Sélénite, Phénylarséniate, SnCl_4 et MX_2 ; infrarouge et Mössbauer

I - INTRODUCTION

while tetrahedral oxyanions acting as ligands have been extensively reviewed by HATHAWAY (1), the results on the coordination behaviour of pyramidal oxyanions such as selenite and tetrahedral mono-substituted oxyanions such as phenylarsenate are very scarce (2). From our laboratory two selenite derivatives have been reported (3, 4) ; we have also published derivatives and adducts containing tetrahedral oxyanions substituted or not (5 - 10). The aim of this work is to synthesize new selenite and phenylarsenate adducts for determining the coordinating behaviour of the selenite and phenylarsenate oxyanions from the suggested structures.

II - EXPERIMENTAL

Synthesis of $(\text{Me}_4\text{N})_2\text{SeO}_3 \cdot 1/2\text{H}_2\text{O}$ and $\text{R}_4\text{NPhAsO}_3\text{H} \cdot \text{H}_2\text{O}$
($\text{R} = \text{Me}, \text{Et}$) ($\text{L}_1, \text{L}_2, \text{L}_3$)

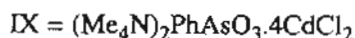
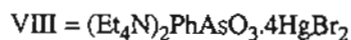
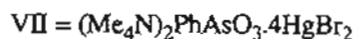
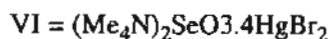
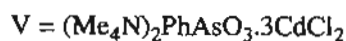
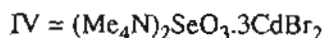
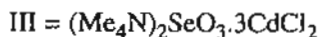
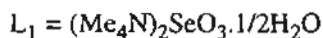
Stoichiometric amounts of a 25% water solution of R_4NOH ($\text{R} = \text{Me}, \text{Et}$) and H_2SeO_3 (98%) or PhAsO_3H_2 (all purchased from Merck chemicals) were mixed. The solution was slightly heated and stirred about one hour and water removed in vacuo at 60°C . The resulting powders were recrystallized from absolute ethanol.

2.1 - Synthesis of complexes and derivatives

The white precipitates obtained on mixing a benzene or an ethanolic solution of the halides with an ethanolic solution of L_1, L_2 or L_3 in defined ligand to metal ratio, were stirred during more than two hours, filtered and washed with hot ethanol.

The elemental analyses performed by the "Service Central d'Analyses" C. N. R. S., Vernaison, France, are reported on table 1 with the ligand to metal ratio.

The i. r. and Mössbauer spectra were obtained as reported in (11) (the non solubility of the title compounds has prevent to carry their NMR study).



Ligands and adducts	Ligand to metal ratio	%C	%H	%N	%X	%M
L ₁	-	34.69 (34.50)	09.17 (09.08)	09.52 (09.65)	- (-)	- (-)
L ₂	-	40.96 (40.63)	06.82 (06.67)	04.77 (04.63)	- (-)	- (-)
L ₃	-	48.14 (48.33)	08.20 (08.32)	03.67 (03.80)	- (-)	- (-)
I	1- 1.5	14.41 (14.69)	03.60 (03.84)	04.20 (04.24)	33.98 (34.14)	26.73 (27.07)
II	1-1.5	22.73 (22.51)	03.92 (03.70)	03.79 (03.51)	28.82 (29.05)	24.09 (24.31)
III	1- 4	11.63 (11.49)	02.90 (02.82)	03.39 (03.09)	25.81 (25.78)	40.86 (40.40)
IV	1- 4	08.78 (08.56)	02.20 (02.37)	02.56 (02.47)	43.93 (44.39)	30.87 (30.85)
V	1- 1	18.70 (19.05)	03.22 (03.42)	03.11 (02.98)	23.71 (23.28)	37.54 (37.47)
VI	1- 4	05.59 (05.63)	01.39 (01.41)	01.63 (01.66)	- (-)	46.70 (46.72)
VII	1- 4	09.38 (09.52)	01.62 (01.75)	01.56 (01.63)	- (-)	44.81 (44.51)
VIII	1- 4	13.88 (13.67)	02.36 (02.50)	01.47 (01.52)	- (-)	42.17 (42.00)
IX	1-4	15.53 (15.37)	02.68 (02.76)	02.99 (02.89)	26.26 (26.45)	41.57 (41.34)

Table 1 : Analytical data

2.2 - Mössbauer data

I. S. is the isomer shift, Q. S. the nuclear quadrupole splitting and G the linewidth. The isomer shift is related to the density around the tin center while the Q. S. measures the deviation from perfect spherical environment (the Q. S. of SnCl_6 is zero).

$(\text{Me}_4\text{N})_2\text{SeO}_3 \cdot (\text{SnCl}_4)_{1.5}$ I.S. = 0.26mms^{-1} ; Q.S. = 0.41mms^{-1} ; $G \approx 1.12$

$(\text{Me}_4\text{N})_2\text{PhAsO}_3 \cdot (\text{SnCl}_4)_{1.5}$ I.S. = 0.21mms^{-1} ; Q.S. = 0.48mms^{-1} ; $G = 0.89$

III - RESULTS AND DISCUSSION

General considerations

The selenite SeO_3 (C_{3v} symmetry) has four vibrations: ν_1 : the symmetric stretching vibration of A_1 type non degenerate, ν_3 : the anti-symmetric stretching vibration, E type doubly degenerate, ν_4 : the anti-symmetric bending doubly degenerate E Type, ν_2 : the symmetric bending vibration of A_1 type non degenerate.

When the selenite belongs to C_{3v} point group (in the case of a free or a tri O bonding selenite) these vibrations appear as one band. When the selenite is monocoordinated or symmetrically bicoordinated, the point group becomes C_s and C_1 when the bicoordination is not symmetrical: in these two cases the E type vibrations (ν_3 and ν_4) split into two bands of A' and A'' type.

When the anion is monosubstituted this type of correlation does not work.

In the table 2 are reported the i. r. data of the title adducts with the symmetry of the selenite.

$(\text{Me}_4\text{N})_2\text{AO}_3 \cdot (\text{SnCl}_4)_{1.5}$ (A = Se, PhAs) (I, II)

Because of the non splitting of ν_3 and ν_4 we can clearly conclude to the presence of a selenite of C_{3v} symmetry in the adduct I. TUDELA and al. reported in (12) the Mössbauer data of cis and trans $\text{SnCl}_4 \cdot 2\text{L}$ isomers ; all the cis O-coordinated isomers have Q. S. values lower

than 0.57mms^{-1} . The Q. S. values of I and II falling in the range of the Q. S. values of the cis O-coordinated isomers allows us to conclude to the presence of cis coordinated SnCl_4 . The I. S. values of I and II are in the range defined by TUDELA and al. (14) for O_2SnCl_4 frameworks. The i. r. and Mössbauer data allow to conclude to an infinite layered structure with tridentate ligand and cis coordinated SnCl_4 for I and II (Figure a)

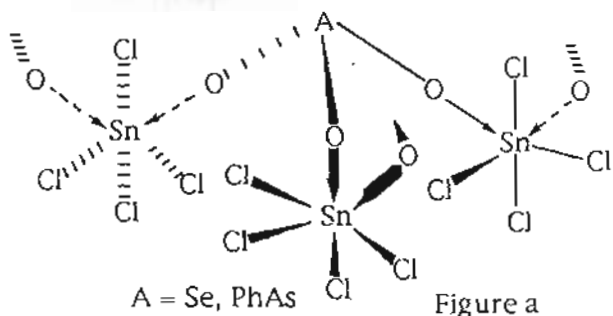


Table 2

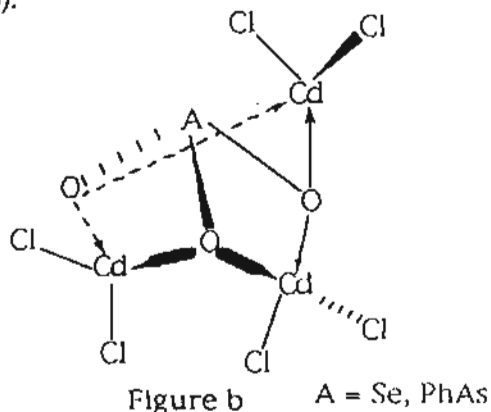
Adducts	νAO_3	δAO_3	νMO	νMX_2	Sym. SeO_3^{2-}
I	860m(v ₁) 723s(v ₃)	551m	-	300s	C _{3v}
II	880vs	355m	223m	302vs	
III	810w(v ₁) 721vs(v ₃)	496s(v ₄) 370m(v ₂)	249sh	207vs	C _{3v}
IV	830w(v ₁) 723vs(v ₃)	498m(v ₄) 370m(v ₂)	238w	154vs	C _{3v}
V	865vs 806sh 790s	431vs 380m 329w	242sh	205vs	
VI	810m(v ₁) 721vs(v ₃) 661vs(v ₃)	489m(v ₂) 377m(v ₄) 408vs(v ₄)	235sh	187vs	C ₃ ou C ₁
VII	839s 825s 786vs	411w 362w 348m	227w	187vs	
VIII	870w 830m 790s 770w	421m 374s 310m	272s	191vs	
IX	865vs 810m 790m	416m 393m 350m	228sh	202vs	

ν_{AsC} is localized as a very strong band around 690cm^{-1} . Phenyl and cations bands are arbitrary omitted.

$(\text{Me}_4\text{N})_2\text{A} \cdot 3\text{CdX}_2$ (A = SeO_3 , PhAsO_3 ; X = Cl, Br) (III, IV, V)

The i. r. data of the selenite CdX_2 adducts indicate C_{3v} symmetry for the selenite (non splitting of ν_3 and ν_4); the appearance of ν_{CdO} at 249 cm^{-1} and 238 cm^{-1} in the i. r. spectra of the selenite adducts indicates coordination between the cadmium and the selenite oxyanion.

A discrete structure is suggested with a trichelatant selenite or phenylarsenate on the hypothesis of a tetrahedral environment around the metal (this type of environment is present in adducts of formulae $(\text{R}_4\text{N})_2\text{SO}_4 \cdot 2\text{CdX}_2$ (R = Me, Et, X = Cl, Br) which contain a Td symmetry sulfate and a tetrahedral environment around the metallic centers) (8) (Figure b).



$(\text{R}_4\text{N})_2\text{A} \cdot 4\text{MX}_2$ (A = SeO_3 , PhAsO_3 ; M = Hg, Cd; X = Cl, Br) (VI, VII, VIII, IX)

The splitting of ν_3 of the selenite into two bands at 721cm^{-1} and 661 cm^{-1} in the i. r. spectrum of the selenite adduct indicates C_s or C_1 symmetry for the selenite. The presence of bands due to ν_{MO} indicates ligand to metal coordination.

A discrete structure is suggested with a tetrachelatant ligand and a tetrahedral environment around the metal centers (Figure c).

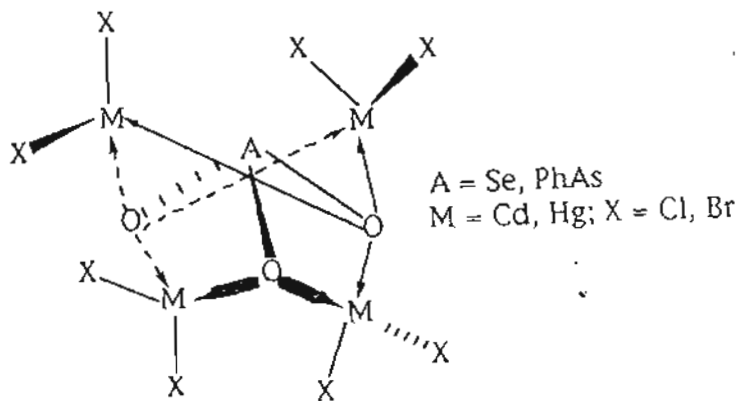


Figure c

IV - CONCLUSION

The SnCl_4 adducts have a polymeric structure with an octahedral environment around the tin (IV) center, SnCl_4 being cis coordinated and the oxyanions behaving as tridentate ligands. The polychelant nature of both the selenite and the phenylarsenate oxyanions in the MX_2 adducts is noteworthy.

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