

**NEW MONO AND POLYNUCLEAR DIMETHYLARSENIATO,
HYPOPHOSPHITO, DIPHENYLPHOSPHINATO MX_2 ADDUCTS
AND $Me_2AsO_2SnMe_3$: SYNTHESIS AND INFRARED STUDY**

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Résumé : $Me_2AsO_2SnMe_3$ et de nouveaux complexes diméthylarséniato, hypophosphito et diphenylphosphinato d'halogénures de cadmium, de mercure et de zinc ont été synthétisés et leurs analyses élémentaires effectuées. L'étude par spectroscopie infrarouge a permis de proposer des structures discrètes ou en chaîne infinie avec des anions chélatants et / ou poly-uidentes.

Mots clés : infrarouge, complexes diméthylarséniato, hypophosphito et diphenylphosphinato, ligands polydentates.

I - INTRODUCTION

The main results on oxyanions acting as ligands has been reported by Hathaway (1). Potier and Rosolovskii groups have extensively studied the behaviour of ClO_4^- as ligand (2-9). In the framework of our research work on the coordinating ability of tetrahedral oxyanions, some papers on non substituted oxyanions (SO_4^{2-} , SeO_4^{2-} , MoO_4^{2-} and WO_4) have been reported (10-14). In this paper dealing with the coordinating behaviour of the tetrahedral disubstituted oxyanions $Me_2AsO_2^-$, $H_2PO_2^-$ and $Ph_2PO_2^-$, we report the synthesis and the i. r. study of some new dimethylarseniato, hypophosphito and diphenylphosphinato CdX_2 , ZnX_2 and HgX_2 ($X = Cl, Br$) adducts.

II- EXPERIMENTAL

The salts $\text{H}_2\text{PO}_2\text{NMe}_4 \cdot \text{H}_2\text{O}$, $\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot \text{H}_2\text{O}$, $\text{Ph}_2\text{PO}_2\text{NMe}_4 \cdot \text{H}_2\text{O}$ and $\text{Ph}_2\text{PO}_2\text{NEt}_4 \cdot 2\text{H}_2\text{O}$ were obtained by mixing a water solution of tetramethylammonium hydroxide 25% or tetraethylammonium hydroxide 10% with $\text{H}_2\text{PO}_2\text{H}$, $\text{Me}_2\text{AsO}_2\text{H}$ and $\text{Ph}_2\text{PO}_2\text{H}$ (purchased from Merck) in 1 : 1 ratio. The white powder obtained after evaporation is recrystallized in absolute ethanol.

The mixtures of ethanolic solutions of these salts with the metal halides give white precipitates stirred during some hours, filtered off, washed with hot ethanol and dried in vacuo.

The elemental analyses were performed by the "Service Central d'Analyses" C.N.R.S. Vernaison- FRANCE, the i. r. spectra scanned as Nujol mulls on a Perkin- Elmer 580 infrared spectrophotometer ($4000 - 200 \text{ cm}^{-1}$) and FTIR NICOLET spectrophotometer ($600 - 50 \text{ cm}^{-1}$) using CsI or polyethylene windows. The NMR study of the metals has not been carried because of the non solubility of these compounds in current NMR solvents.

On the Table 1 are reported the elemental analyses data with the salt to metal halide ratio in parentheses. Found (Calculated), X = Cl, Br ; M = Hg, Sn

adducts	C	H	N	X	M
H ₂ PO ₂ NMe ₄ .H ₂ O	30.52 (30.57)	8.75 (8.92)	8.85 (8.92)		
Me ₂ AsO ₂ NMe ₄ .H ₂ O	31.52 (31.45)	8.85 (8.74)	6.23 (6.11)		
Ph ₂ PO ₂ NMe ₄ .H ₂ O	62.26 (62.13)	7.86 (7.76)	4.62 (4.53)		
Ph ₂ PO ₂ NEt ₄ .2H ₂ O	62.54 (62.66)	8.76 (8.87)	3.72 (3.65)		
H ₂ PO ₂ NMe ₄ .CdBr ₂	11.66 (11.68)	3.35 (3.43)	3.50 (3.40 ^o)	38.61 (38.85)	
Ph ₂ PO ₂ NMe ₄ ZnCl ₂	44.24 (44.93)	5.39 (5.14)	3.40 (3.27)	16.58 (16.68)	
Me ₂ AsO ₂ NMe ₄ .2HgCl ₂	9.55 (9.55)	2.28 (2.48)	1.95 (1.85)	18.64 (18.80)	
Me ₂ AsO ₂ NMe ₄ .2HgBr ₂	7.71 (7.73)	1.90 (1.94)	1.56 (1.50)		43.21 (43.05)
Me ₂ AsO ₂ NMe ₄ .3CdCl ₂	9.45 (9.46)	2.44 (2.38)	2.02 (1.84)	27.68 (27.95)	
2Me ₂ AsO ₂ NMe ₄ .3CdBr ₂	11.62 (11.63)	2.80 (2.92)	2.26 (2.26)	38.66 (38.69)	
2H ₂ PO ₂ NMe ₄ .3CdBr ₂	8.76 (8.77)	2.61 (2.57)	2.60 (2.55)	43.59 (43.78)	
2Ph ₂ PO ₂ NEt ₄ .3CdBr ₂	31.02 (31.76)	4.13 (3.97)	1.80 (1.85)	31.52 (31.76)	
Et ₄ N(Ph ₂ PO ₂) ₃ Zn.ZuCl ₂	53.81 (53.75)	5.12 (5.09)	1.46 (1.42)	7.45 (7.22)	
Et ₄ N(Ph ₂ PO ₂) ₃ Zn.ZuBr ₂	49.07 (49.07)	4.69 (4.66)	1.36 (1.30)	12.10 (12.10)	
(Me ₄ N) ₂ (Me ₂ AsO ₂) ₄ Cd.4CdCl ₂	12.45 (12.40)	3.09 (3.13)	1.74 (1.81)	18.41 (18.39)	
Me ₂ AsO ₂ SnMe ₃	19.84 (19.96)	4.74 (4.99)	- (-)	- (-)	39.61 (39.48)

Analytical Data

III - RESULTS AND DISCUSSION

i. r. symbols : *vas* : antisymmetrical stretching vibration, *vs* : symmetrical stretching vibration, δ : symmetrical bending vibration, ρ : rocking vibration, ω : wagging vibration

i. r. abbreviations : (s): strong, (v.s.): very strong, (m): medium, (w): weak

Infrared data

Let us consider the assignments of the *i. r* spectra made using the published spectroscopic data (15-18) and ours *i. r.* spectra of $\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot \text{H}_2\text{O}$ and $\text{Ph}_2\text{PO}_2\text{NR}_4 \cdot n\text{H}_2\text{O}$ ($\text{R} = \text{Me}, \text{Et}$; $n = 1, 2$).

$\text{H}_2\text{PO}_2\text{NMe}_4 \cdot \text{CdBr}_2$: 2408 cm^{-1} (w) *vs* PH_2 2380 cm^{-1} (m) *vas* PH_2 1175 cm^{-1} (m) δPH_2 1140 cm^{-1} (m) *vas* PO_2 1092 cm^{-1} (w) ωPH_2 1062 cm^{-1} (m) *vs* PO_2 810 cm^{-1} (s) ρPH_2 455 cm^{-1} (m) δPO_2 241 cm^{-1} (w) *vCdO* 178 cm^{-1} (v.s.) *vCdBr}_2.*

$\text{Ph}_2\text{PO}_2\text{NMe}_4 \cdot \text{ZnCl}_2$: 1158 cm^{-1} , 1131 cm^{-1} (v.s.) *vas* PO_2 1056 cm^{-1} (v.s.) *vs* PO_2 765 cm^{-1} (s) *vas* PC_2 703 cm^{-1} (w) *vs* PC_2 564 cm^{-1} (s), 535 cm^{-1} (m) δPO_2 389 cm^{-1} (w) δPC_2 277 cm^{-1} (v.s.) *vZnCl}_2* 220 cm^{-1} (sh) *vZnO*.

$\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot 2\text{HgCl}_2$: 832 cm^{-1} (m) *vas* AsO_2 790 cm^{-1} (s) *vs* AsO_2 645 cm^{-1} (m) *vas* AsC_2 605 cm^{-1} (w) *vs* AsC_2 401 cm^{-1} (m) *dAsO}_2* 356 cm^{-1} (s) *vHgCl}_2* 316 cm^{-1} (m) ρAsO_2 285 cm^{-1} (w) *dAsC}_2* 258 cm^{-1} (m) *nHgO*.

$\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot 2\text{HgBr}_2$: 815 cm^{-1} (m) *vas* AsO_2 790 cm^{-1} (s) *vs* AsO_2 640 cm^{-1} (m) *vas* AsC_2 605 cm^{-1} (w) *vs* AsC_2 405 cm^{-1} (v.s.) *dAsO}_2* 316 cm^{-1} (v.s.) ρAsO_2 235 cm^{-1} (s) *vHgBr}_2* 213 cm^{-1} (m) *vHgO*

$\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot 3\text{CdCl}_2$: 840 cm^{-1} (s) *vas* AsO_2 788 cm^{-1} (s) *vs* AsO_2 650 cm^{-1} (m) *vas* AsC_2 605 cm^{-1} (w) *vs* AsC_2 419 cm^{-1} (s) δAsO_2 365 cm^{-1} (m) *vAsO}_2* 291 cm^{-1} (w) δAsC_2 241 cm^{-1} (w) *vCdO* 201 cm^{-1} (v.s.) *vCdCl}_2.*

$2\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot 3\text{CdBr}_2$: $837\text{cm}^{-1}(\text{v.s.})$ vasAsO_2 $785\text{cm}^{-1}(\text{v.s.})$
 vsAsO_2 $650\text{cm}^{-1}(\text{m})$ vasAsC_2 $605\text{cm}^{-1}(\text{w})$ vsAsC_2 $400\text{cm}^{-1}(\text{s})$ dAsO_2
 $322\text{cm}^{-1}(\text{m})$ rAsO_2 $288\text{cm}^{-1}(\text{w})$ δAsC_2 $235\text{cm}^{-1}(\text{w})$ vCdO $177\text{cm}^{-1}(\text{v.s.})$
 vCdBr_2 .

$2\text{H}_2\text{PO}_2\text{NMe}_4 \cdot 3\text{CdBr}_2$: $2418\text{cm}^{-1}(\text{m})$ vsPH_2 $2407\text{cm}^{-1}(\text{m})$
 vasPH_2 $1180\text{cm}^{-1}(\text{m})$ δPH_2 $1140\text{cm}^{-1}(\text{m})$ vasPO_2 $1105\text{cm}^{-1}(\text{s})$ ωPH_2
 $1065\text{cm}^{-1}(\text{s})$ vsPO_2 $825\text{cm}^{-1}(\text{s})$ ρPH_2 $455\text{cm}^{-1}(\text{m})$ δPO_2 $177\text{cm}^{-1}(\text{v.s.})$
 vCdBr_2 $235\text{cm}^{-1}(\text{w})$ vCdO .

$2\text{Ph}_2\text{PO}_2\text{NEt}_4 \cdot 3\text{CdBr}_2$: $1185\text{cm}^{-1}(\text{m})$, $1175\text{cm}^{-1}(\text{m})$ vasPO_2
 $1035\text{cm}^{-1}(\text{m})$ vsPO_2 $753\text{cm}^{-1}(\text{s})$ vasPC_2 $702\text{cm}^{-1}(\text{w})$ vsPC_2 $563\text{cm}^{-1}(\text{s})$,
 $545\text{cm}^{-1}(\text{m})$ δPO_2 $366\text{cm}^{-1}(\text{m})$ δPC_2 $287\text{cm}^{-1}(\text{m})$ vCdO $178\text{cm}^{-1}(\text{v.s.})$
 vCdBr_2 .

$\text{Et}_4\text{N}(\text{Ph}_2\text{PO}_2)_3 \cdot 3\text{ZnCl}_2$: $1210\text{cm}^{-1}(\text{v.s.})$, $1130\text{cm}^{-1}(\text{v.s.})$ vasPO_2
 $1050\text{cm}^{-1}(\text{v.s.})$ vsPO_2 $763\text{cm}^{-1}(\text{s})$ nasPC_2 $703\text{cm}^{-1}(\text{s})$ vsPC_2
 $555\text{cm}^{-1}(\text{v.s.})$, $540\text{cm}^{-1}(\text{v.s.})$ δPO_2 $390\text{cm}^{-1}(\text{m})$ δPC_2 $310\text{cm}^{-1}(\text{v.s.})$
 vZnCl_2 $245\text{cm}^{-1}(\text{w})$ vZnO .

$\text{Et}_4\text{N}(\text{Ph}_2\text{PO}_2)_3 \cdot 3\text{ZnBr}_2$: $1205\text{cm}^{-1}(\text{v.s.})$, $1160\text{cm}^{-1}(\text{m})$ vasPO_2
 $1050\text{cm}^{-1}(\text{v.s.})$ vsPO_2 $761\text{cm}^{-1}(\text{s})$ nasPC_2 $701\text{cm}^{-1}(\text{v.s.})$ vsPC_2
 $548\text{cm}^{-1}(\text{s})$, $535\text{cm}^{-1}(\text{s})$ δPO_2 $387\text{cm}^{-1}(\text{s})$ δPC_2 $231\text{cm}^{-1}(\text{m})$ vZnO
 $215\text{cm}^{-1}(\text{v.s.})$ vZnBr_2 .

$(\text{Me}_4\text{N})_2(\text{Me}_2\text{AsO}_2)_4 \cdot 4\text{CdCl}_2$: $840\text{cm}^{-1}(\text{s})$ vasAsO_2 $790\text{cm}^{-1}(\text{v.s.})$
 vsAsO_2 $645\text{cm}^{-1}(\text{m})$ vasAsC_2 $602\text{cm}^{-1}(\text{w})$ vsAsC_2 $407\text{cm}^{-1}(\text{s})$ dAsO_2
 $330\text{cm}^{-1}(\text{w})$ ρAsO_2 $291\text{cm}^{-1}(\text{w})$ δAsC_2 $218\text{cm}^{-1}(\text{m})$ $241\text{cm}^{-1}(\text{sh})$
 vCdO $208\text{cm}^{-1}(\text{v.s.})$ vCdCl_2 .

$\text{Me}_2\text{AsO}_2\text{SnMe}_3$: $845\text{cm}^{-1}(\text{v.s.})$ nasAsO_2 $735\text{cm}^{-1}(\text{v.s.})$ nsAsO_2
 $640\text{cm}^{-1}(\text{s})$ vasAsC_2 $600\text{cm}^{-1}(\text{m})$ vsAsC_2 562cm^{-1} vasSnC_3 $430\text{cm}^{-1}(\text{s})$
 δAsO_2 $330\text{cm}^{-1}(\text{m})$ ρAsO_2 $300\text{cm}^{-1}(\text{m})$ δAsC_2 $250\text{cm}^{-1}(\text{m})$ vSnO .

On all the spectra of these complexes, the presence of the bands due to ν_{MO} indicates the coordination between the anion and the metallic centers.

It is well known that a correlation exists between the number of bands on the infrared spectra and the symmetry of the anion in the case of tetrahedral non substituted anions such as sulfate, selenate, phosphate,.... but this correlation does not work with substituted tetrahedral oxyanions (19) : in this specific case of the anions of $R_2As(P)O_2$ -type if we consider the PO_2 coordinating group the two stretching vibrations are non degenerate and it is impossible to differentiate between the monocoordinating and the polycoordinating anion because in all the cases we obtain the same number of bands due to the absence of degenerate vibrations and splitting (in the cases where many bands appear for a non degenerate vibration they are always due to solid state effects which increase the number of bands because of the involvement of the number of molecules per unit cell ; in fact every molecule has its own vibrations and coupling between the different vibrations gives a multiplicity of bands in cases where only one non degenerate band was expected).

In all the following structures of MX_2 adducts, the environment of the metal is supposed mainly tetrahedral (rather than trigonal) as in $(Me_4N)_2SO_4 \cdot 2CdCl_2$ (13) which contains a T_d symmetry anion and a tetrahedral environment around the metallic centers.

$H_2PO_2NMe_4 \cdot CdBr_2$ and $Ph_2PO_2NMe_4 \cdot ZnCl_2$

Two structures are possible : a discrete structure with monochelating anion (fig.1a) and an infinite chain with a bi-unidentate anion (fig.1b).

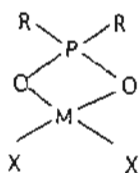


figure 1a

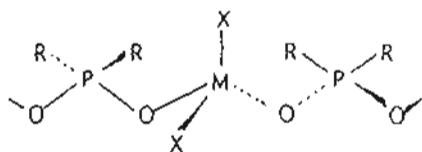


figure 1b

M = Zn, Cd
X = Cl, Br
R = H, Ph

$Me_2AsO_2NMe_4 \cdot nMX_2$ (n = 2, 3 ; M = Hg, Cd ; X = Cl, Br)

For the adduct $\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot 3\text{CdCl}_2$, two discrete structures can be suggested : one with a bridging and monochelating anion with two types of CdCl_2 (fig.2a), the other one with only chelated CdCl_2 molecules involving the chlorides (fig.2b).

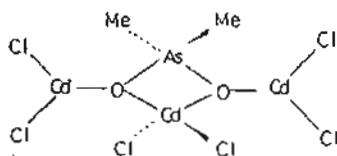


figure 2a

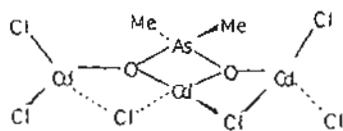


figure 2b

For the adducts $\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot 2\text{HgX}_2$ ($\text{X} = \text{Cl}, \text{Br}$) we suggest a discrete structure with a bichelating anion (fig. 3).

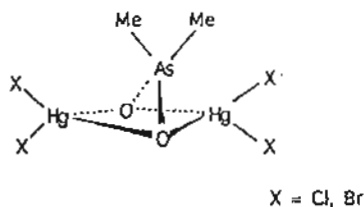


figure 3

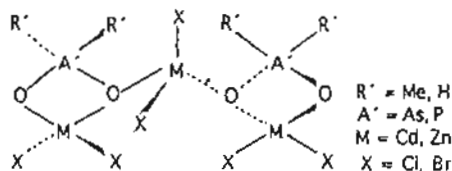


figure 4

$2\text{R}'_2\text{A}'\text{O}_2\text{NR}_4 \cdot 3\text{MX}_2$ ($\text{R}' = \text{H}, \text{Me}, \text{Ph}$; $\text{A}' = \text{As}, \text{P}$; $\text{R} = \text{Me}, \text{Et}$; $\text{M} = \text{Cd}, \text{Zn}$; $\text{X} = \text{Cl}, \text{Br}$)

These adducts can be considered as two molecules of $\text{Me}_2\text{AsO}_2\text{NMe}_4 \cdot \text{CdBr}_2$, $\text{H}_2\text{PO}_2\text{NMe}_4 \cdot \text{CdBr}_2$ or $\text{Ph}_2\text{PO}_2\text{NEt}_4 \cdot \text{ZnCl}_2$ sharing one CdBr_2 or ZnCl_2 molecule. The structure suggested is discrete with a mono-chelating and unidentate anion (fig.4).

$\text{Et}_4\text{N}(\text{Ph}_2\text{PO}_2)3\text{Zn} \cdot \text{ZnX}_2$ ($\text{X} = \text{Cl}, \text{Br}$)

The more symmetrical structure consist of a dimer $(\text{ZnXPh}_2\text{PO}_2)_2$ linked to $\text{Ph}_2\text{PO}_2\text{NEt}_4$, the Zn centers having a tetrahedral environment (fig.5).

1.4CdCl₂

be considered as (Me₄N)₂(Me₂AsO₂)₄Cd coordinated to 2 molecules. (Me₄N)₂Cd(Me₂AsO₂)₄ can be considered as (Me₄N)₂CdCl₄ in which the chlorides has been substituted by uncoordinating Me₂AsO₂⁻. The suggested structure is discrete with monochelating and unidentate anions (fig. 6). (two Cd-O distances involving two bands due to νCdO)

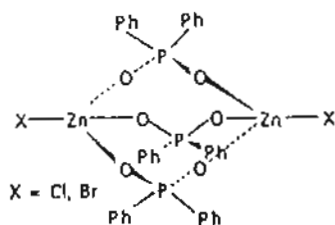


figure 5

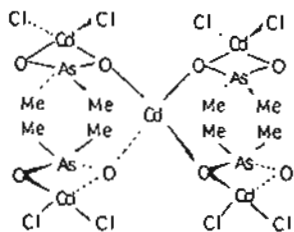


figure 6

Me₂AsO₂SnMe₃

In the infrared spectrum of this derivative, the absence of the band around 515 cm⁻¹ due to νSnC₃ is a clear indication of planar SnMe₃ residue because in planar SnC₃ skeleton (D_{3h} symmetry) this vibration of A₁ symmetry is inactive. From these data we suggest an infinite chain structure with a bridging anion, the environment around the tin center being a trigonal bipyramid (this structure is similar to c type structure of SnR₃A derivatives (R = Alkyl or Aryl ; A = oxyanion) according to TIEKINK (20).

IV - CONCLUSION

In these adducts the anions behave as chelating ligands mainly (with or without some additional monocoordinations) or bridging ligands in some cases.

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