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SYNTHESIS, NMR AND MASS SPECTROMETRIC INVESTIGATION OF A NEW MULTINUCLEAR SILVER(I) COMPLEX WITH PHOSPHORUS-, SULFUR-CONTAINING LIGAND

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SYNTHESIS, NMR AND MASS SPECTROMETRIC INVESTIGATION OF A NEW MULTINUCLEAR SILVER(I) COMPLEX WITH PHOSPHORUS-, SULFUR-CONTAINING LIGAND

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The new multinuclear coordination compound $[\text{Ag}_3(\text{LH})_2]\text{NO}_3$ (where L is $\text{Ph}_2\text{P}(\text{S})\text{CH}_2\text{P}(\text{S})\text{Ph}_2$) was synthesized by deprotonation of the complex AgLNO_3 with Et_3N . On the basis of ^1H and ^{31}P NMR spectroscopic data combined with a mass spectrometric examination in FD and FAB variants the complexation $[\text{Ag}(\text{L}-\text{H})_2]^+$ was presumed to consist of a metallomacrocyclic unit $[\text{Ag}_2(\text{LH})_2]$ with an unsymmetrically coordinated third silver(I) ion. The ligand within the complex was found to undergo hydrolysis and redox reactions in the gas phase under FD and FAB conditions.

Keywords: Multinuclear silver(I) complex; di(phosphinosulfate); deprotonation

INTRODUCTION

Silver(I) ions as 'soft' electron acceptors are known to form stable complexes with ligands containing 'soft' sulfur donor atoms.¹ In particular, the thiophosphoryl-containing ligands - di(phosphinosulfides) were found to be effective complexants and extractants toward silver salts² giving chelate coordination compounds AgLNO_3 and AgL_2NO_3 . In those complexes Ag^+ ions are coordinated, respectively, to two or four sulfur atoms of $\text{PS}=\text{}$ groups. One of the di(phosphinosulfides) used was bis(diphenylthiophosphoryl)methane; in the present paper it will be referred to as L.

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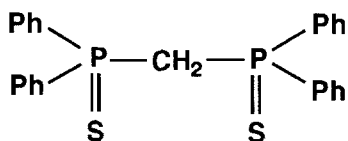
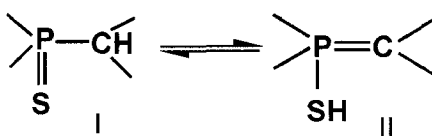


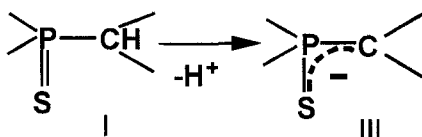
Chart L

Phosphine sulfides, are believed to similarly to thioketones, be capable of existing in two tautomeric forms - thiophosphoryl (I) and mercaptoylide (II),³ but because of the low PS = group basicity the tautomeric equilibrium (Scheme (1)) for the majority of thiophosphoryl-containing compounds is shifted to structure (I).



Scheme (1)

One possible way to stabilize a mercaptoylide form of a phosphine sulfide is to bind the thiol sulfur atom with a transition metal ion. The known synthetic route toward such substances includes, as the first stage, deprotonation of the starting phosphine sulfide yielding thiolate product (III):



Scheme (2)

In particular, di(phosphinosulfide) L (pK 19.7⁴) was deprotonated by *n*-butyl lithium.⁵ The compound thus obtained interacted with salts of some transition metals to give bis(methinodithiophosphinate) chelate complexes:

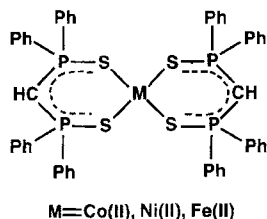


Chart IV



Scheme (3)

The above substances are sensitive to moisture and decompose in air. No complex of this ligand with metal ions in an oxidation state other than (+2) were reported. Nevertheless, one could expect silver(I) cations to also be capable of stabilizing the deprotonated ligand form $(\text{L}-\text{H})^-$ by coordination.

The alternative route to coordination compounds of $(\text{L}-\text{H})^-$ derives from the assumption that bonding of the thiophosphoryl sulfur atoms of L to a 'soft' metal cation (Ag^+ in particular) leads to an increase in acidity of the methylene group of di(phosphinosulfide).

In that case deprotonation of the coordinated ligand L might occur under more gentle conditions than for the 'free' one, for instance on treatment of the complex with Et_3N .

The present research studies the possibility of obtaining silver(I) complexes of the deprotonated ligand $(\text{L}-\text{H})^-$ starting from known coordination compounds AgLNO_3 and AgL_2NO_3 and to examine the structure and properties of the obtained products by NMR and mass spectrometry.

EXPERIMENTAL

Reagents and Instrumentation

Bis(diphenylthiophosphoryl)methane (L) was synthesized as described in the literature.⁶ Complexes of bis(diphenylthiophosphoryl)methane (L)- AgLNO_3 and AgL_2NO_3 were prepared as previously described.²

A WP-200 'Bruker' spectrometer was used for ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. The conductometry determinations were performed with P5010 alternate current bridge with the cell constant value 0.20.

Field desorption (FD) mass spectra were recorded with an MI 1201 mass spectrometer. A thin current conducting tungsten thread with a gold dendrite-shaped cover was used as the ion emitter. The details of the experiment can be found elsewhere.⁷

The FAB analysis was performed with an MX 1310 high resolution mass spectrometer previously described⁸ with the use of Ar atoms for bombardment, and glycerine as a matrix.

Synthesis of $\text{Ag}_3(\text{L-H})_2\text{NO}_3$

Bis(diphenylthiophosphoryl)methane (L) (0.045 g; 0.1 mmol) was dissolved in anhydrous chloroform (3 mL). On addition of AgNO_3 (0.017 g; 0.1 mmol), the mixture was stirred until complete dissolution. 1 drop (about 0.2 mmol) of Et_3N was then added. In some minutes small colorless crystals of the complex precipitated. The product was filtered off, washed with chloroform and dried in vacuum. Yield 20%; m.p.(decomp.) 150°C . *Anal.* Calcd. for $\text{C}_{50}\text{H}_{42}\text{NO}_3\text{P}_4\text{S}_4\text{Ag}_3$ (%): C 46.84; H 3.12; N 1.09; Ag 25.27. Found: C 46.75; H 3.07; N 1.07; Ag 25.20. The substance is highly sensitive to moisture and light.

RESULTS AND DISCUSSION

Interaction of the complex compounds AgLNO_3 and AgL_2NO_3 with Et_3N was studied in anhydrous deuterated acetonitrile and chloroform. Changes in ^1H NMR spectra of the starting complexes were considered to be the evidence of the reaction proceeding.

Addition of Et_3N to the acetonitrilic solution of AgLNO_3 resulted in significant alteration of the ^1H NMR spectrum. In particular, besides the signals relevant to the starting reagents, two multiplets caused by Et_3NH^+ formation⁹ appeared at 1.38 ppm (t) and 3.07 ppm (m.); some more new signals were found in the region of 4.0 ppm and 7.0–8.0 ppm.

The bis-chelate complex AgL_2NO_3 appeared to be unreactive toward Et_3N as no measurable changes in the ^1H NMR spectra were observed. Evidently, deprotonation of the ligand within the complex requires some reconstruction of the coordination unit. Probably, stability of the bis-chelate tetrahedral AgL_2NO_3 is too high² for rearrangement to take place under mild conditions. On the other hand, failure to deprotonate might result from an insufficient increase in methylene group acidity on coordination of two molecules of the ligand L to one silver(I) ion.

When the reaction of AgLNO_3 with Et_3N was carried out in chloroform, colorless crystalline substance was obtained, an elemental analysis for which corresponds to the formula $\text{Ag}_3(\text{L-H})_2\text{NO}_3$. Since the substance is unstable to moisture and light, crystal structure studies for this complex are troublesome. Indirect data obtained from spectroscopic investigations have been used in this work.

The ^1H NMR spectrum of $\text{Ag}_3(\text{L-H})_2\text{NO}_3$ dissolved in CD_3CN is different from the spectrum of AgLNO_3 . The ratio of the signals of aromatic and aliphatic protons for the ligands in the newly formed compound is 20:1 in contrast with 20:2 in AgLNO_3 , confirming deprotonation of L. The triplet signal in the spectrum of AgLNO_3 ($\delta=4.27$

p.p.m.; $J_{HP}=13.0$ Hz) caused by absorption of CH_2 protons transformed, in the case of $Ag_3(L-H)_2NO_3$, into two triplets close in intensity, but different in the spin-spin coupling constant values ($\delta=4.32$ p.p.m.; $J_{HP}=12.9$ Hz and $\delta=3.97$ ppm; $J_{HP}=8.4$ Hz, respectively). The presence of two triplets corresponding to $-CH=$ protons indicates inequivalence of the methyne groups of two $(L-H)^-$ particles within the complex. The 1H NMR spectrum of $AgLNO_3$ in the phenyl region also changed dramatically on ligand deprotonation. Besides two multiplets (δ 7.56 and 7.86 ppm) similar to those recorded for $AgLNO_3$, there are three additional signals (δ 7.01, 7.31 and 8.07 ppm) in the spectrum of $Ag_3(L-H)_2NO_3$, indicating that the new compound contains more inequivalent aromatic protons. In other words, unlike in the case of $AgLNO_3$, phenyl substituents at phosphorus atoms in $Ag_3(L-H)_2NO_3$ differ.

The $^{31}P\{^1H\}$ NMR spectrum of $Ag_3(L-H)_2NO_3$ contrasts with that of $AgLNO_3$ ($\delta=37.99$ ppm, s.) with two singlets (δ 42.80 and 38.75 ppm). The absence of spin-spin coupling indicates that both phosphorus atoms of the ligand are equivalent. Hence, the existence of two signals results from distinction between two $(L-H)^-$ ligands in the complex. This is consistent with the observed inequivalence of methyne groups of the ligand and may be caused by an unsymmetrical location of three silver(I) ions relative to two $(L-H)^-$ ligands in the coordination sphere of $Ag_3(L-H)_2NO_3$.

A FD and FAB mass spectrometric investigation of the multinuclear compound was performed to define the molecular mass of the complex in order to confirm the composition, and also to study its transformations under high field influence and on the fast atom bombardment. The data obtained are given in the Table I.

TABLE I FD and FAB mass spectra of $[Ag_3(L-H)_2]NO_3$

FD		FAB		Attribution**
<i>m/e</i>	Relative Intensity, % [#]	<i>m/e</i>	Relative Intensity, %	
107	0.6	107; 109	14.0	Ag^+
109	0.4			
225	0.6			S_7
		246; 248	2.3	Ag_2S
256	0.8			S_8
288	1.5			S_9
		384	1.5	L^d
		400	0.8	L^c
418	6.6	416	1.0	L^b or L^c
432	6.6	432	0.8	L^a
448	7.0	448	9.3	L
		490; 492	0.8	$(AgL^d)^+$
		507; 509	1.5	$(AgL^c)^+$
		524; 526	6.5	$(AgL^b)^+$ or $(AgL^c)^+$
557	6.6	555; 557	9.3	$(AgL)^+$
		663; 665	3.1	$[Ag_2(L-H)]^+$

TABLE I (Continued)

FD		FAB		Attribution ^{##}
<i>m/e</i>	Relative Intensity, % [#]	<i>m/e</i>	Relative Intensity, %	
893	7.0	878; 880	0.8	(AgL ^d) ⁺
		890; 892	0.5	(AgL ^d L ^e) ⁺
		906; 910	0.8	(AgL ^c L ^d) ⁺ or (AgL ^e) ⁺
940	9.3	940; 942	2.3	(AgL ^b) ⁺ or (AgL ^e) ⁺
		957; 959	0.6	(AgL ^a L ^b) ⁺
				(AgLL ^b) ⁺ or (AgL ^a) ⁺ or (AgLL ^c) ⁺
1002	11.8	1005; 1007	6.0	(AgL ^c) ⁺
		1044; 1046	8.4	(AgL ^b) ⁺
1110	12.9			[Ag ₂ (L-H) ₂]
1218	18.5	1215–1220	10.8	[Ag ₃ (L-H) ₂] ⁺
1280	2.4	1278–1282	18.9	[Ag ₃ (L-H) ₂]NO ₃

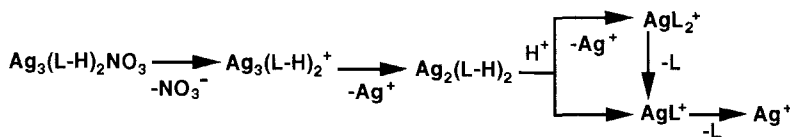
[#]Relative intensities at 200°C.

^{##}The designations L^a, L^b, L^c, L^d, L^e are given in the text.

The FD was conducted at an emitter temperature varying between 150–350°C. In this temperature interval FD spectra of the complex contained weak ion peaks corresponding to the molecular ion of the compound Ag₃(L-H)₂NO₃ (*m/e* 1280), and also peaks of high intensity which can be attributed to the cation Ag₃(L-H)₂⁺ (*m/e* 1218).

Analysis of the FD mass spectra showed fragmentation of the multinuclear complex Ag₃(L-H)₂NO₃ to proceed according to Scheme (4):

An ion peak observed at *m/e* = 1110 is caused by formation of Ag₂(L-H)₂ which appears on loss of one Ag⁺ cation from the starting complex. Deprotonated ligand ions (L-H)⁻ in the coordination compound are capable of interacting with water molecules present at the emitter,¹⁰ giving rise to protonation of the multinuclear complex followed by its destruction yielding the mononuclear complexes AgL⁺ and AgL₂⁺. Fragmentation in high field results in free ligand L and silver(I) cations.



Scheme (4)

Comparison of the FD and FAB mass spectra for Ag₃(L-H)₂NO₃ indicates that both in high electric field and on fast atom bombardment fragmentation of the multinuclear complex occur by Scheme (4). It is noteworthy that instead of an ion peak for Ag₂(L-H)₂ present in the FD spectra, the FAB mass spectrum contains an intensive peak at *m/e* 663–665 corresponding to Ag₂(L-H)⁺. Possibly,

under FAB ionization conditions unlike in the case of high field ionization, $\text{Ag}(\text{L}-\text{H})$ is easier to break off from $\text{Ag}_3(\text{L}-\text{H})_2^+$ than one of three Ag^+ cations.

All attempts to extract one of the silver ions from $\text{Ag}_3(\text{L}-\text{H})_2\text{NO}_3$ by chemical means were unsuccessful. In particular, no AgCl precipitation occurred when the multinuclear complex was acted upon with Et_4NCl or Bu_4NCl in acetonitrile or chloroform solutions, proving all three Ag^+ cations are incorporated in the coordination sphere of the complex. As the molar conductivity value in CH_3CN for the substance studied is $1.70 \times 10^2 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, this compound is a 1:1 electrolyte.¹¹

Therefore, the multinuclear complex formula can be written as $[\text{Ag}_3(\text{L}-\text{H})_2]\text{NO}_3$. It is assumed to contain a 12-membered metallomacrocylic structural fragment $\text{Ag}_2(\text{L}-\text{H})_2$ where silver(I) ions are bound to the ligand *via* sulfur donor atoms. The arrangement of this fragment might be similar to that established for the silver(I) diethyl dithiophosphate complex $[\text{Ag}\{\text{S}_2\text{P}(\text{OEt})_2\}_2]_2^{2-}$.¹² This complex contains a centrosymmetric eight-membered ring composed of two Ag atoms bound by two dialkyl dithiophosphate groups acting simultaneously as bridging and chelating ligands. In our opinion, the third Ag^+ cation in $[\text{Ag}_3(\text{L}-\text{H})_2]^+$ is coordinated unsymmetrically to $\text{Ag}_2(\text{L}-\text{H})_2$ producing the inequivalence of ligands in the complex. Possibly, it is bonded to both sulfur atoms of one of $(\text{L}-\text{H})^-$ species as represented below.

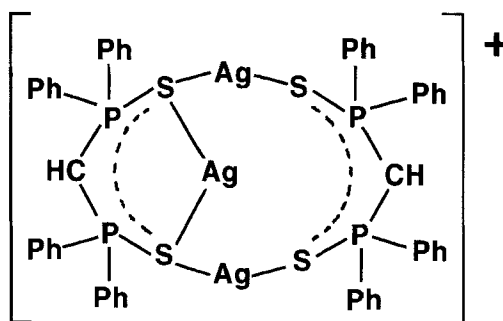


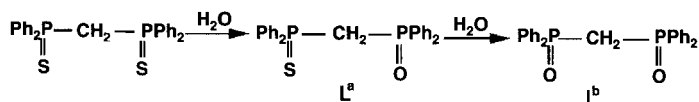
Chart V

Analysis of the mass spectra of $[\text{Ag}_3(\text{L}-\text{H})_2]\text{NO}_3$ showed that the fragmentation given in the Scheme (4) does not complete all possible transformations of the complex taking place under strong electric field action and on fast Ar atoms bombardment. A number of chemical reactions were found to occur in the gas phase.¹³

Both FD and FAB mass spectra of the multinuclear complex contain peaks with m/e values significantly exceeding 1280. These might result from gas phase

association reactions in the system. Another possible explanation is based on the assumption that the multinuclear complex under research is a polymer with $[\text{Ag}_3(\text{L-H})_2]\text{NO}_3$ being an elementary unit of the polymer.

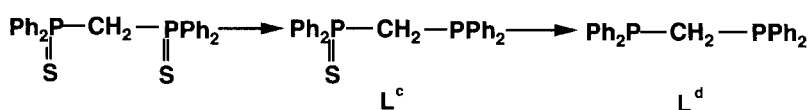
Phosphine sulfides are known to hydrolyze to give corresponding phosphine oxides.¹⁴ Di(phosphinosulfide) L, on complete or partial hydrolysis, can form L^a and L^b :



Scheme (5)

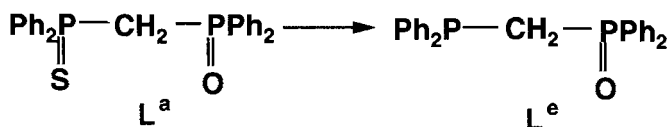
Indeed, FD mass spectra of $[\text{Ag}_3(\text{L-H})_2]\text{NO}_3$ contain ion peaks corresponding to L^a and L^b , and also to silver(I) complexes of those compounds (see Table I). At the same time, despite the presence of peaks in the mass spectra confirming hydrolytic reactions for L and its complexes, no silver sulfide formation was observed. Evidently, in the gaseous phase sulfide undergoes oxidation to sulfur(0). FD mass spectra of the multinuclear complex contain peaks which can be attributed to S_7 , S_8 , and S_9 . Both silver(I) and phosphorus(V) could be the oxidizing agent.

Phosphine sulfides can be reduced to phosphines much easier than for similar phosphine oxides. It is possible that under the experiment conditions L is completely or partially reduced by sulfide ions present in the system:



Scheme (6)

and also



Scheme (7)

And finally, having assumed formation in the gas phase of reduction products of the ligand L (L^c , L^d , L^e), one can expect the presence of silver(I) complexes

of those compounds. Really, several suitable ion peaks were recorded in FD mass spectra of $[\text{Ag}_3(\text{L}-\text{H})_2]\text{NO}_3$, namely, $m/e=418(\text{L}^c)$, 893 ($[\text{AgL}^d\text{L}^e]^+$), 940 ($[\text{AgL}^c\text{L}^e]^+$), 972 ($[\text{AgLL}^c]^+$).

FAB mass spectrometry differs from FD not only in ionization method, but also in the presence of glycerine as a matrix. Since glycerine itself undergoes fragmentation and transformation on Ar atom bombardment, gas phase reactions of substances studied by this method must recognize these reactions.

In general, the main difference between FAB and FD mass spectra for $[\text{Ag}_3(\text{L}-\text{H})_2]\text{NO}_3$ consists in the number of ion peaks relevant to products of side hydrolysis reactions of the ligand within the complex. Evidently, under the FAB experimental conditions the di(phosphinosulfide) undergoes hydrolysis to a higher extent due to interaction with traces of water present in glycerine or with hydroxide ions resulting from fragmentation of glycerine molecules. Unlike in the FD spectra of the complex under investigation, a moderate peak of Ag_2S is present in the FAB spectra.

Another peculiarity of FAB spectra of $[\text{Ag}_3(\text{L}-\text{H})_2]\text{NO}_3$ is containing more ion peaks that can be attributed to products of reduction reactions in the gas phase. To illustrate, along with peaks in the region of m/e values 940, 892, 418 which are common for both kinds of mass spectra, several moderate ion peaks relevant to complexes of diphosphine L^d , phosphinophosphine sulfide L^c and phosphinophosphine oxide L^e were found in the FAB spectra along with weak peaks of free reduced ligands (see Table I). Apparently, redox reactions under FAB in the system are encouraged by the presence of glycerine ionization products possessing high reduction ability, hydrogen radicals are one possibility.¹⁵

Acknowledgments

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