

SYNTHESIS AND CHARACTERIZATION OF CATIONIC ASTATINE
COMPOUNDS WITH SULPHUR-CONTAINING LIGANDS STABLE IN
AQUEOUS SOLUTIONS

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The formation of cationic astatine compounds with thiourea, thiourea derivatives and some N-acylthioureas was investigated in aqueous solutions. The ion mobilities in free electrolytes were determined for the detection of carrier-free astatine compounds and their characterization. Informations about the stability of this group of compounds could be given after investigations in the presence of halogenide and pseudo halogenide ions $/Cl^-$, Br^- , I^- , SCN^- /. First results on the reaction of $At/\theta/+$ with thiourea derivatives and N-acylthioureas in acid and neutral solutions are reported. The cationic astatine compound formation with representatives of this group is shown.

INTRODUCTION

Visser¹ has been the first who reported on the compound formation of astatine with thiourea /THS/ and thioacetamide /TAA/. He supposed a stoichiometry of $At/THS/2^+$ and $At/TAA/2^+$

similar to the iodine compounds^{2,3}. The astatine thiourea complex formation was confirmed by electromigration studies in aqueous solutions⁴. Under the same conditions a compound formation of thioacetamide could not be proved.

Experiments showed that $\text{At}/\theta/^{+}$ reacts also with other thiourea derivatives and N-acylthioureas. In this publication we report on the synthesis, chemical behaviour and stability of astatine compounds with sulphur-containing ligands. The characterization of the parent compounds and the reaction products were carried out by electromigration studies under various conditions.

EXPERIMENTAL

Production of ^{211}At

^{211}At was obtained via $/\alpha,2n/$ reaction on natural bismuth with 28 MeV α -particles in the Rossendorf cyclotron U-120. After thermochromatographic reprocessing of the bismuth target, we received ^{211}At in 0.2 ml H_2O /Ref. 5/.

Synthesis

$\text{At}/\theta/^{+}$:

A mixture of 0.05 ml $\text{At}^{\text{O}}.\text{H}_2\text{O}$ and 0.05 ml 0.1N HNO_3 +0.01M $\text{K}_2\text{Cr}_2\text{O}_7$ was heated at 373 K for 5 min.

AtX_2^{-} :

0.05 ml solution, containing $\text{At}/\theta/^{+}$ was added to 0.05 ml 1N HX; $\text{AtX}_2^{-}/\text{X}=\text{Cl}^{-}, \text{Br}^{-}, \text{SCN}^{-}/$ was found.

At^{-} :

0.05 ml $\text{At}^{\text{O}}.\text{H}_2\text{O}$ and 0.05 ml 5% $\text{N}_2\text{H}_4.\text{H}_2\text{O}$ were heated at 373 K for 5 min.

The characterization of $\text{At}/\theta/^{+}$ and AtX_2^{-} was carried out by ion mobility measurements.

Cationic compounds of At/θ^+ with thiourea, thiourea derivatives and N-acylthioureas could be obtained by different ways:

1. By the addition of 10-20 μl of At/θ^+ -containing solution to electrolytes used for electromigration measurements containing the complexing agent.
2. Recomplexation of AtCl_2^- by the method mentioned above.
3. Mixing 0.02 ml $\text{At}^{\circ}.\text{H}_2\text{O}$ with 0.02 ml 0.5N HCl and 0.01M $\text{K}_2\text{Cr}_2\text{O}_7$ solution and recomplexation of the formed AtCl_2^- by the addition of an aliquot of the solution, containing a sulphur-containing complexing agent.
4. Mixing At^- with a solution, containing 0.02M HClO_4 and the complexing agent.

The measurements of the ion mobilities in different free electrolytes were carried out by the method described in Refs 6,7.

RESULTS AND DISCUSSION

Some data on cationic astatine compounds with sulphur-containing ligands are summarized in Table 1. The ion mobility of the astatine thiourea complex is $2.5 \pm 0.1 \times 10^{-4}$ $\text{cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$ at 298 ± 0.5 K and an ion strength of $0.05 \text{ mol} \cdot \text{l}^{-1}$. Substituted thioureas show lower ion mobilities. Ion mobilities, given in Table 1, are average results of 5-8 measurements. Experiments in the presence of 0.02M HCl doubtlessly confirm the formation of cationic At/θ^+ compounds with the corresponding ligands.

In the absence of a complexing agent At/θ^+ reacts immediately with Cl^- to form AtCl_2^- . Electromigration investigations in electrolytes, which contain complexing agents and halogenides, hint at the stability of the asta-

TABLE 1
 Ion mobilities of different cationic At/I/-compounds with thiourea and thioourea derivatives as ligands
 T = /298±0.5/ K

Substance	Composition of electrolyte						Ion mobility
	C _{Ligand} x10 ³ , mol.l ⁻¹	C _{HClO₄} x10 ² , mol.l ⁻¹	C _{NaClO₄} x10 ² , mol.l ⁻¹	C _{HCl} x10 ² , mol.l ⁻¹	U _{Cation} x10 ⁴ , cm ² , v ⁻¹ .s ⁻¹		
<chem>H2N-C(=S)-NH2</chem>	2.5	2.0	3.0	-	+ /2.48±0.08/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /2.44±0.09/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /2.42±0.10/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /2.17±0.08/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /1.79±0.06/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /1.82±0.03/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /1.88±0.09/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /1.97±0.12/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /1.80±0.06/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /1.82±0.11/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /1.56±0.08		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /1.43±0.12/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /1.85±0.28/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /1.75±0.25/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /1.75±0.10/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /1.54±0.13/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /1.45±0.12/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /1.33±0.10/		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	2.0	3.0	-	+ /1.54±0.12		
<chem>CH3-N(C(=S)-NH2)-H</chem>	2.5	-	3.0	2.0	+ /1.53±0.22/		

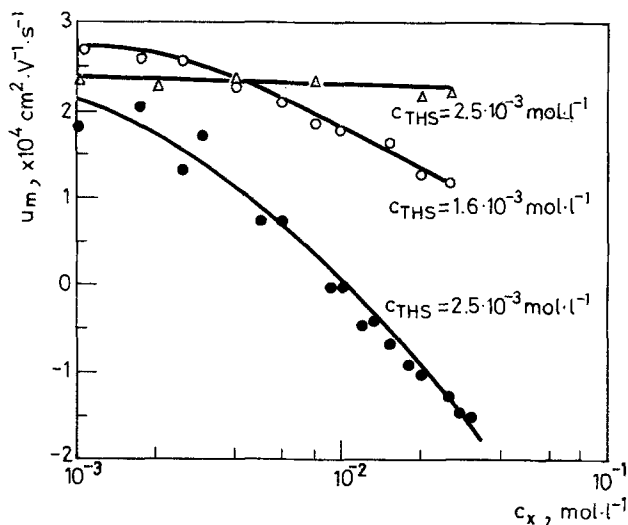


Fig. 1. Electromigration behaviour of the At/I/-thiourea-complex in dependence of the concentration of thiourea and of X^- / $X = \Delta Cl^-$, $o SCN^-$, $\bullet I^-$;
 $T = 298 + 0.5/K$; $\mu = 0.05 \text{ mol.l}^{-1}$

tine thiourea compounds and compounds with further ligands. Figure 1. shows the results.

It has been found that the ion mobility of the cationic astatine thiourea complex does not depend on the thiourea concentration. We established that the complex is stable at $298 \pm 5 \text{ K}$ both in the presence of the complexing agent and in the presence of NaClO_4 solution in acidic and neutral solutions. Results are summarized in Fig. 2.

In Table 2 are given the first results about the chemical behaviour of At/θ^+ with N-acylthioureas and other ligands.

The cationic complexes exist also in the presence of HCl . Their ion mobilities fit into the trend of the ion mobilities of compounds mentioned in Table 1.

From the results the following conclusions can be drawn:

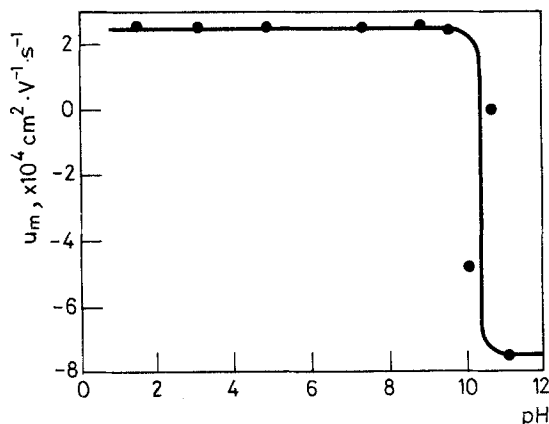
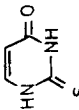
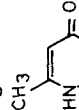
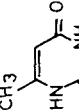
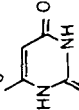
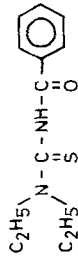
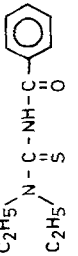
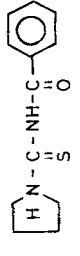
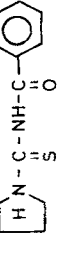
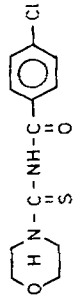
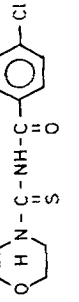


Fig. 2. Ion mobilities of the At/I/-thiourea complex in dependence of the pH-value $T = /298+0.5/K$; $\mu = 0.05 \text{ mol.l}^{-1}$; electrolyte = HClO_4 , NaClO_4 , NaOH ; thiourea = 0.02 mol.l^{-1}

- The ion mobility of the $\text{At}/\theta/^{+}$ -thiourea complex at $298 \pm 0.5 \text{ K}$ and at an ion strength $\mu = 0.05 \text{ mol.l}^{-1}$ fits into the series of the monovalent astatine compounds as $[\text{At}(\text{H}_2\text{O})_2]^{+}$, $\text{AtX}_2^{+} / \text{X} = \text{Cl}^{-}, \text{Br}^{-}, \text{I}^{-}, \text{SCN}^{-}, \text{C}/\text{CN}/_3^{-}, \text{N}_3^{-}$ characterized till now⁸⁻¹².
- The composition of the $\text{At}/\theta/^{+}$ -thiourea complex is assumed to be $[\text{At}(\text{THS})_2]^{+}$.
- Starting from $[\text{At}(\text{THS})_2]^{+}$ we found that the ion mobility decreases when a ligand of higher molecular mass is bound to At^{+} . For the N-acylthioureas it is in the range of $1 \times 10^{-4} / \text{cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$. A composition similar to the thiourea complex is probable.
- The ion mobilities of these new cationic astatine compounds are independent of the ligands concentration in a wide range.
- The compounds are much more stable than AtI_2^{-} , the most stable astatine compound known till now.

TABLE 2

Ion mobilities of the cationic At/I/-compounds with N-acyl-thioureas and further sulphurcontaining ligands. T = /298±0.5/K

Substance	Composition of electrolyte					Ion mobility
	C _{Ligand} , x10 ³ , mol.l ⁻¹	C _{HClO₄} , x10 ² , mol.l ⁻¹	C _{NaClO₄} , x10 ⁻² , mol.l ⁻¹	C _{HCl} , x10 ⁻² , mol.l ⁻¹	^u Cation x10 ⁴ , cm ² .V ⁻¹ .s ⁻¹	
	saturated	2.0	3.0	-	+ / 2.40 ± 0.06 /	
	saturated	-	3.0	2.0	+ / 0.70 ± 0.02 /	
	saturated	2.0	3.0	-	+ / 2.45 ± 0.12 /	
	saturated	-	3.0	2.0	+ / 2.42 ± 0.08 /	
	2.5	2.0	3.0	-	+ / 1.38 ± 0.23 /	
	2.5	-	3.0	2.0	+ / 0.80 ± 0.12 /	
	2.5	2.0	3.0	-	+ / 1.15 ± 0.29 /	
	2.5	-	3.0	2.0	+ / 1.00 ± 0.21 /	
	2.5	2.0	3.0	-	+ / 0.76 ± 0.21 /	
	2.5	-	3.0	2.0	+ / 0.83 ± 0.19 /	

Experiments with thioacetamide, thioglycolic acid and thioacetanilide used as ligands were not successful. In all cases an anion was detected in 0.02N HClO₄ + 0.03M ligand containing solutions. Its ion mobility corresponded to the mobility of At⁻ at the same ion strength.

The complex formation of At/θ/⁺ with sulphur-containing complexing agents correspond to Pearson's theory.

Preliminary experiments of the reaction of At/θ/⁺ with selenonurea derivatives proved that cationic astatine compounds are also formed with this group of compounds¹³.

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