EFFECT OF METAL COORDINATION ON THE SEPARATION PROCESS IN ION MOBILITY CELL

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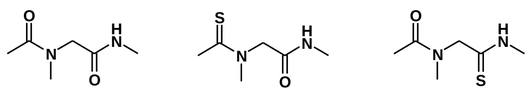
OVERVIEW

- Peptoid (1) and its thio-analogues (2 and 3) as simple model compounds.



(1) (2) (3)

- Travelling wave ion mobility spectrometry – used to measure collision cross sections of selected ions.
- Influence of the metal cation (Li^+, Na^+, K^+, Cu^+, Ag^+) on the separation of selected peptoid and thiopeptoids in ion mobility cell is examined.

INTRODUCTION

Ion mobility (IM) mass spectrometry is a method that allows separation between ions on the basis of ion-neutral collision cross-section, which in turn is related to the structure of the ion. The potential application of ion mobility mass spectrometry to distinguish between many types of ions such as isomers, isobars, and conformers is related, *inter alia*, to the resolution power of the ion mobility mass spectrometer. In this preliminary work, the effect of the metal coordination on the separation process of peptoid (1) and thiopeptoids (2 and 3) is examined.

The study is a part of the project focuses on the examination of structural properties of thioxopeptoids as potential building blocks in the synthesis of biologically active compounds.

METHODS

- IMS measurements and data processing:

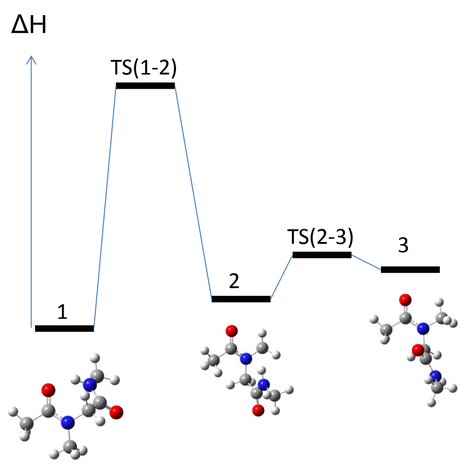
Traveling-wave IM experiments were performed using a Waters Synapt G2-S HDMS instrument equipped with an electrospray ion source. The collision cross sections of analyzed ions were calculated on the basis of calibration curve of reference quaternary ammonium cations.

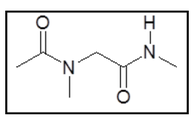
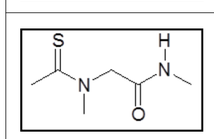
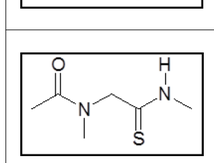
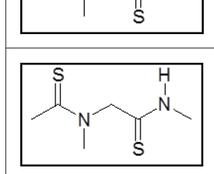
- Calculations:

Gaussian 09 program; Mobcal[1]

RESULTS

Figure 1. Conformational energy diagram for neutral peptoids and thiopeptoids.



Compound	Structure	ΔH [kJ/mol]
	1	0
	2	8.5
	3	15.9
	TS (1-2)	**67.4**
	TS (2-3)	19.6
	1	0
	2	8.9
	3	18.3
	TS (1-2)	**85.5**
	TS (2-3)	20.6
	1	0
	2	12.4
	3	24.4
	TS (1-2)	**75.7**
	TS (2-3)	26.1
	1	0
	2	12.4
	3	25.8
	TS (1-2)	**85.1**
	TS (2-3)	27.3

(B3LYP/6-311++G(2d,p))

Figure 2. Example of ion mobility separation of sodiated ions.

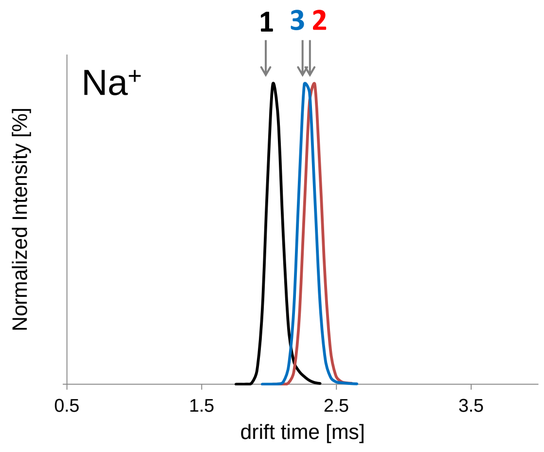
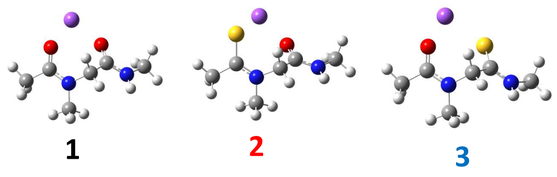


Figure 3. Optimized structures of sodiated ions.



	Distance [Å]	
Ion	O---Na	O (S)---N
1	2.18256	2.20684
2	2.19231	2.70327
3	2.16575	2.74281

Table 1. Experimental vs. theoretical collision cross sections of reference ions.

Quaternary Amines	Measured Ω [Å²]	Theoretical * Ω [Å²]		
		PA	EHSS	TJ
tetramethylammonium	48.5	51.6	53.32	46.0
tetraethylammonium	65.9	70.2	73.4	65.1
tetrapropylammonium	88.9	94.1	100.7	90.8
tetrabutylammonium	111.2	116.3	126.7	114.5

*) Collision cross sections calculated within this work (M05-2X/6-31+g(d,p)).

Table 2. Theoretical vs. measured collision cross sections of sodiated ions.

Ion	Theoretical Collision Cross Sections Ω [Å²]			Measured Collision Cross Sections Ω [Å²]	
	PA	EHSS	TJ	a)	b)
1 + Na^+	76.5	80.4	69.5	72.8	77.0
2 + Na^+	81.9	86.2	71.8	78.9	83.3
3 + Na^+	80.9	84.8	70.1	77.9	82.2

a) Experimental collision cross sections of reference ions taken from literature.[2]
b) Collision cross sections of reference ions calculated within this work (M05-2X/6-31+g(d,p), from projection approximation values).

Table 3. Measured collision cross sections of peptoids and thiopeptoids coordinated to selected metal cations.

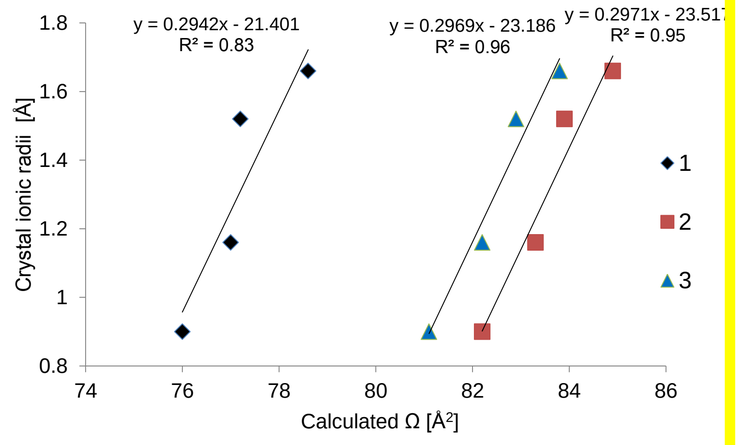
Compound	Collision Cross Sections Ω [Å²] a)						Compound	b)					
	Li^+	Na^+	K^+	Rb^+	Cu^+	Ag^+		Li^+	Na^+	K^+	Rb^+	Cu^+	Ag^+
1	72.0	72.8	73.0	74.4	76.0	78.9	**1**	76.0	77.0	77.2	78.6	80.2	83.3
2	77.5	78.9	79.5	80.5	76.3	79.6	**2**	82.2	83.3	83.9	84.9	80.6	84.0
3	76.4	77.9	78.5	79.4	76.5	78.9	**3**	81.1	82.2	82.9	83.8	80.0	83.3

a) Experimental collision cross sections of reference ions taken from literature.[2]
b) Collision cross sections of reference ions calculated within this work (M05-2X/6-31+g(d,p),from projection approximation values).

CONCLUSIONS

- Neutral peptoid (1) and its thio-analogues (2 and 3) have similar structures of stable conformers, however thiopeptides have the higher barrier for conversion between conformers (Figure 1).
- In comparison to neutral peptoid (1) and thiopeptoids (2 and 3), the coordination to metal cation leads to only one stable conformer (Figure 3).
- Collision cross-sections vary for metal cation adducts (Table 3).
- Project approximation method (PA) proved to be in better agreement with the collision cross-section measurements (Table 2).
- Linear relationship between the metal ionic radii and measured collision cross section occurs (Figure 4).

Figure 4. Relationship between measured collision cross section and metal ionic radii (Li^+, Na^+, K^+, Rb^+)[3].



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3. Shannon R. D. "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides". *Acta Cryst*. 1976, A32: 751–767.

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