

Investigation on silver complexes of novel 1,2,3-triazole linked crown ethers by NMR analysis

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Abstract. The novel derivatives of 1,2,3-triazole linked crown ethers were investigated towards silver(I) ion coordination. The NMR measurements in deuterated methanol in different ratios of ligand and silver cation were studied. The experiments were performed in order to examine the way of binding Ag(I) ion by the selected ligands. The results are presented for complexes with the Ag:L stoichiometry 0.5:1, 1:1 and 2:1, respectively. Depending on the type of crown ether moiety incorporated into the macrocyclic skeleton, interesting differences in the mode of stepwise coordination of the ion were noticed.

Keywords. Macrocyclic system; silver complex; 1,2,3-triazole; crown ethers; sulfur compounds

1. Introduction

The synthetic strategy towards macrocyclic systems and the study of their properties have drawn the attention of chemists for many years. It is well known that in the case of preparation, in principle, inter- or intramolecular processes are achieved by usage of high dilution or template methodology. Recently, the click azide–alkyne cycloaddition catalyzed by copper(I) (CuAAC)^{1,2} was implemented as a powerful tool for synthesis of various molecules^{3–5} as well as macrocyclic compounds.^{6–9} The main goal of research in the field of macrocyclic systems is to investigate their properties and potential application in molecular recognition, complexation, catalysis, analysis and construction the modified electrodes, etc.^{10–16}

All of the investigated ligands possess several structural units which can potentially take part in binding of metal cations: oxygen atom donors in polyether crown skeleton, sulfur atoms as soft donors as well as the endocyclic nitrogen atoms of 1,2,3-triazole rings incorporated into the macrocyclic structure. Due to the presence of such different binding sites, these ligands should interact with cations to form stable complexes with alkali metals and alkaline earth metals as well as transition metals.^{17–19} In this paper the preliminary

results of selected macrocycles and the scope of their complexation ability to silver cation are described.

2. Experimental

2.1 Materials

The ligands were synthesized according to the previously described procedure.²⁰ Deuterated methanol (CD₃OD) was purchased from Sigma-Aldrich. Silver(I) nitrate was purchased from Sigma Aldrich and used without further purification.

2.2 Methods

NMR spectra for compounds **L1**, **L2** (figure 1) and their silver (I) complexes were recorded in CD₃OD on a Bruker Avance III 600 spectrometer (¹H-NMR at 600 MHz and ¹³C NMR at 151 MHz) - ¹H NMR spectra of the complexes are shown in electronic Supporting Information (SI) (figures S1–S8). Additionally, HMBC and HMQC spectra of complexes were taken in order to correlate the structural assignments of ligands and are depicted in SI (figures S9–S12). ESI-MS spectra were recorded using a Varian 500-MS LC ion-trap mass spectrometer (Palo Alto, CA, USA). All samples were introduced into the ESI-MS source in continuous infusion by means of the instrument syringe pump at a rate of

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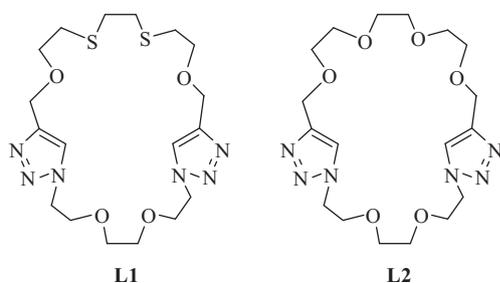


Figure 1. The investigated macrocyclic ligands.

$10 \mu\text{L min}^{-1}$. The ESI-source was operated at 5.00 kV and the capillary heater was set to 300°C . The cone voltage was regulated within the range 50–120 V. Scanning was performed from $m/z = 300$ to 1200.

2.3 Theoretical calculations

All the MD calculations were performed using the TURBOMOLE package.²¹ DFT molecular dynamics calculations were carried out with BLYP functional²² along with triple- ξ valence polarized basis set (TZVP) within the resolution-of-the-identity (RI) approximation.²³

3. Results and Discussion

Selected diazides as well as bis(propargyl) ethers were used as crucial building blocks for the construction of macrocyclic crown ethers and thioethers with built-in 1,2,3-triazole rings^{20,24} (scheme 1).

In the final macrocyclisation step, diazides and terminal bis(alkynes) were reacted in the presence of catalytic amount of copper(I) iodide under the ‘click’ 1,3-dipolar cycloaddition methodology.^{20,24} To obtain the desired products in best yields, high dilution conditions were applied. To the best of our knowledge, the syntheses and properties of such macrocyclic systems, including their sulfur analogues, are little known so far.²⁵

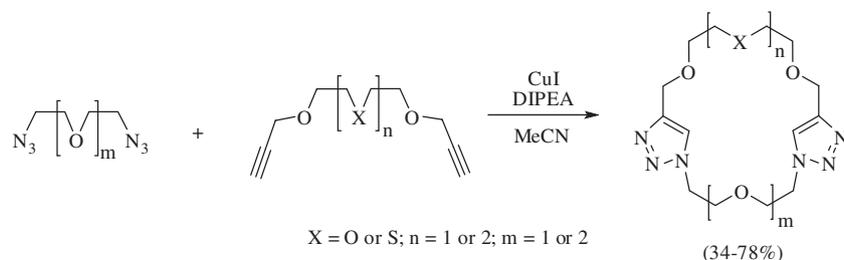
For the present study, two crown derivatives were selected to examine the modes of coordination of silver ions depending on the changes inside the macrocyclic

ring. In one of the selected ligand, two sulfur atoms were incorporated into the polyether moiety instead of oxygen. The complexation properties of this kind of crown compounds have not been studied so far and the presented results can be a good starting point for further detailed research. The investigated ligands **L1** and **L2** are shown in figure 1.

Complexing properties of the ligand **L1** were screened towards binding with silver(I) cations by NMR measurements. To check the ability and mode of binding of silver ions, a series of $^1\text{H-NMR}$ spectra were taken in CD_3OD for the pure ligand **L1** and mixtures obtained after addition of appropriate amounts of silver(I) nitrate to achieve the stoichiometry $\text{Ag}^+:\text{L}$ equal 0.5:1, 1:1, and 2:1. The obtained results are presented in table 1.

In the case of sulfur derivative **L1**, the coordination of silver ion seems to occur at the beginning through the step of coordination binding by sulfur atoms from the macrocyclic chain to form probably sandwich-like complex. Such a conclusion has been drawn from the main shifts of the signals which are observed in macrocyclic moiety near the region when sulfur atoms are incorporated in the chain (figure 2) after addition of the silver ions corresponding to 0.5:1 ($\text{Ag}^+:\text{L1}$) stoichiometry.

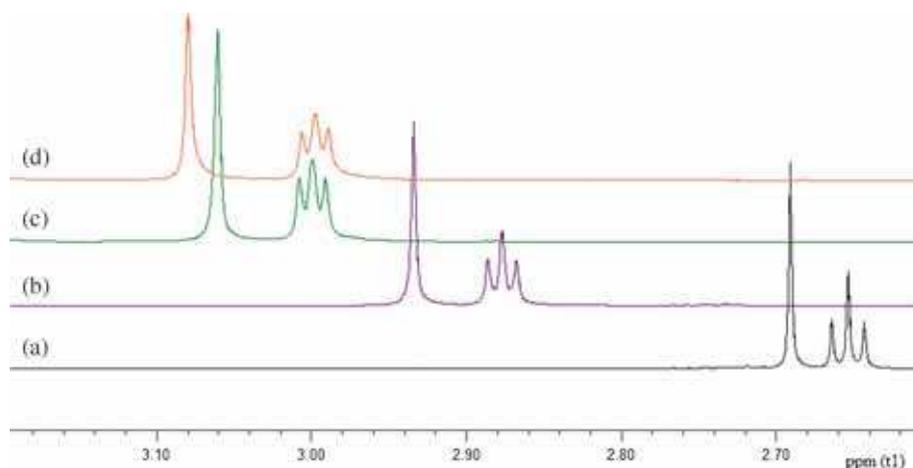
These proton shifts are probably associated with the incorporation of silver cation inside the macrocyclic cavity in the first stage of formation sandwich-like complex and suggests that the metal ion locates out of the plane of macrocyclic ring allowing coordination by the second molecule of the ligand. The very small shift for 1,2,3-triazole ring protons support the above mentioned hypothesis as can be seen from the signals within the region (figure 3, spectra (a) and (b)). Similar sandwich complex for macrocyclic Ag(I) systems were reported in the literature on the basis of potentiometric as well as mass spectrometric measurements.^{19,26,27} Schematic presentation of the sandwich like complex is presented on figure S13 in SI. Although in the ESI-MS spectra there is no signal for the original sandwich complexes, in the spectrum within the region above $m/z = 600$ we can notice two signal pairs at m/z 691–693 and 891–893



Scheme 1. Synthesis of 1,2,3-triazole-linked macrocycles.

Table 1. The ^1H -NMR and ^{13}C -NMR results of complexation of **L1** by silver ion in CD_3OD .

	^1H NMR	^{13}C NMR	
L1	-	145.9	-NC
	7.99, s, 2H	125.8	-CHN
	4.61, s, 4H	64.8	-OC
	4.54, t, 4H, J=5.01 Hz	51.4	-CH ₂ N
	3.82, t, 4H, J=5.08 Hz	70.2	-CH ₂ O
	3.69, t, 4H, J=6.23 Hz	72.2	-OCH ₂
	3.58, s, 4H	71.3	-OC
	2.69, s, 4H	33.7	-SCH ₂ CS
	2.65, t, 4H, J=6.30 Hz	32.2	-CH ₂ S
$\text{Ag}^+:\text{L1}(0.5:1)$	-	145.7	-NC
	7.98, s, 2H	125.3	-CHN
	4.66, s, 4H	64.4	-OC
	4.54, t, 4H, J=4.91 Hz	51.7	-CH ₂ N
	3.83, t, 4H, J=5.02 Hz	70.2	-CH ₂ O
	3.75, t, 4H, J=5.55 Hz	70.2	-OCH ₂
	3.57, s, 4H	71.3	-OC
	2.94, s, 4H	33.6	-SCH ₂ CS
	2.88, t, 4H, J=5.48 Hz	33.6	-CH ₂ S
$\text{Ag}^+:\text{L1}(1:1)$	-	145.8	-NC
	8.00, s, 2H	125.1	-CHN
	4.71, s, 4H	64.1	-OC
	4.57, t, 4H, J=4.78 Hz	52.0	-CH ₂ N
	3.84, t, 4H, J=4.97 Hz	70.2	-CH ₂ O
	3.76, t, 4H, J=4.70 Hz	69.0	-OCH ₂
	3.58, s, 4H	71.4	-OC
	3.06, s, 4H	34.1	-SCH ₂ CS
	3.00, t, 4H, J=5.18 Hz	33.7	-CH ₂ S
$\text{Ag}^+:\text{L1}(2:1)$	-	146.0	-NC
	8.10, s, 2H	125.8	-CHN
	4.73, s, 4H	63.8	-OC
	4.65, t, 4H, J=4.70 Hz	52.4	-CH ₂ N
	3.86, t, 4H, J=4.86 Hz	70.2	-CH ₂ O
	3.70, t, 4H, J=5.08 Hz	68.8	-OCH ₂
	3.60, s, 4H	71.4	-OC
	3.08, s, 4H	34.3	-SCH ₂ CS
	3.00, t, 4H, J=4.95 Hz	34.3	-CH ₂ S

**Figure 2.** The ^1H -NMR spectra of the $-\text{CH}_2\text{-S-CH}_2-$ region in CD_3OD for (a) uncomplexed ligand **L1**, and after adding silver ion with the $\text{Ag}^+:\text{L1}$ molar ratio; (b) 0.5:1; (c) 1:1; and (d) 2:1.

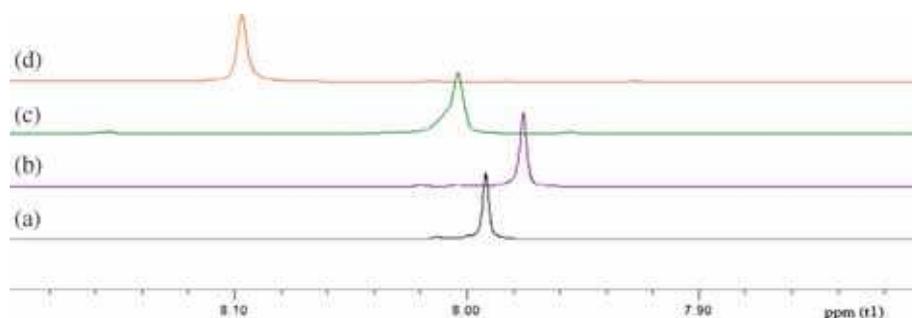


Figure 3. The $^1\text{H-NMR}$ spectra of the 1,2,3-triazole ring proton in CD_3OD for uncomplexed ligand **L1** (a) and after adding silver ion for the $\text{Ag}^+:\text{L1}$ molar ratio; (b) 0.5:1; (c) 1:1; and (d) 2:1.

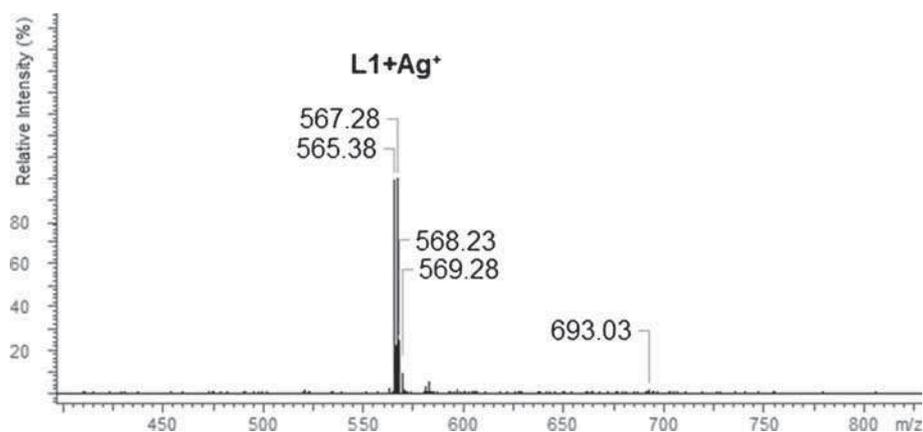


Figure 4. The ESI-MS spectrum of the complexes of **L1** ligand with Ag^+ ions.

which can be attributed to a structure in which one of the macrocyclic rings has been fragmented during the ionization process. The comparison of isotope patterns of the signals show the presence of the silver ion in the structure. This fact can be used as indirect proof of the existence of the sandwich-like complex.

Further shift of $-\text{CH}_2\text{S}-$ protons after addition of the next portion of silver ions (figure 3, spectrum (c)) suggests that after achieving 1:1 stoichiometry, the silver ions are nested inside the macrocyclic cavity but still have no interaction with the nitrogen atoms from 1,2,3-triazole subunits (figure 3 (a),(b) and (c)). The ESI-MS spectrum of the investigated system shows signal at m/z 565.38 with the characteristic isotopic pattern (figure 4). The interesting fact in the case of silver (I) complex with this ligand is that during the MS experiment no typical additional complexes with Na^+ or K^+ ions were observed and there was no signal of parent ligand at m/z 459.60. Such a behavior is typical for deeply nested metal cation inside the macrocyclic cavity forming very stable complexes.

Finally, the last portion of the silver ions was added which corresponds to the stoichiometry of 2:1 of

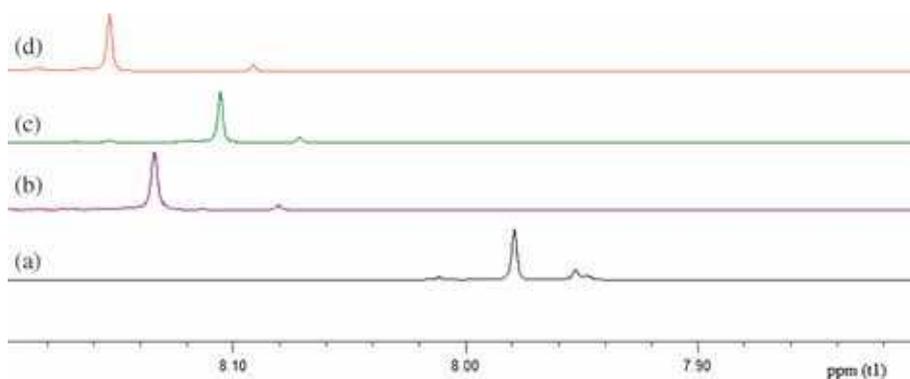
$\text{Ag}^+:\text{L1}$. The spectrum (d) showed the downfield shift by 0.1 ppm of the protons for 1,2,3-triazole ring (from 8.00 to 8.10 ppm) and the proton shift within the region assigned for the $\text{CH}_2\text{-N}$ moiety (from 4.57 to 4.65 ppm) was also observed. This kind of behavior indicates that the way of binding of the second silver ion is supported by the nitrogen atoms of 1,2,3-triazole rings in the macrocyclic structure. Due to the good stabilization of the 1:1 complex, the ESI-MS measurements showed only a very weak signal at m/z 337.37 ($\text{RT} \ll 1\%$). During the ionization process, the second silver ion is easily removed from the structure forming the most stable 1:1 complex.

Subsequently, the complexation of silver cation by ligand **L2** was monitored by NMR. The results collected in table 2 indicate that the way of complexation is significantly different in comparison with that observed for the sulfur derivative **L1**.

In the first step the coordination seems to occur through the nitrogen atoms of the 1,2,3-triazole rings what can be connected with the significant downfield shifts of protons from the CHN region (figure 5, spectrum (b)).

Table 2. The ^1H -NMR and ^{13}C -NMR results of complexation of **L2** by silver ion in CD_3OD .

	^1H NMR	^{13}C NMR
L2	-	146.2
	7.98 (s, 2H, -CHN)	125.8
	4.63 (s, 4H, -OCH ₂ C)	65.1
	4.53 (t, J=5.01 Hz, 4H, -CH ₂ N)	51.8
	3.83 (t, J=5.08 Hz, 4H, -CH ₂ O)	70.2
	3.68 (t, J=6.23 Hz, 4H, -CH ₂ O)	70.8
	3.67 (s, 4H, -O(CH ₂) ₂ O)	71.6
	3.59 (s, 4H, -OCH ₂)	71.2
	3.57 (s, 4H, -O(CH ₂) ₂ O)	71.2
$\text{Ag}^+:\text{L2}(0.5:1)$	-	146.6
	8.13 (s, 2H, -CHN)	125.8
	4.77 (s, 4H, -OCH ₂ C)	65.0
	4.62 (t, J=4.93 Hz, 4H, -CH ₂ N)	51.8
	3.83 (t, J=4.83 Hz, 4H, -CH ₂ O)	70.1
	3.68 (t, J=5.02 Hz, 4H, -CH ₂ O)	70.8
	3.67 (s, 4H, -O(CH ₂) ₂ O)	71.6
	3.66 (s, 4H, -OCH ₂)	71.2
	3.59 (s, 4H, -O(CH ₂) ₂ O)	71.2
$\text{Ag}^+:\text{L2}(1:1)$	-	146.6
	8.11 (s, 2H, -CHN)	125.7
	4.76 (s, 4H, -OCH ₂ C)	64.6
	4.59 (t, J=4.88 Hz, 4H, -CH ₂ N)	51.8
	3.83 (t, J=4.79 Hz, 4H, -CH ₂ O)	70.0
	3.68 (t, J=5.08 Hz, 4H, -CH ₂ O)	70.8
	3.67 (s, 4H, -O(CH ₂) ₂ O)	71.6
	3.64 (s, 4H, -OCH ₂)	71.2
	3.59 (s, 4H, -O(CH ₂) ₂ O)	71.2
$\text{Ag}^+:\text{L2}(2:1)$	-	146.7
	8.15 (s, 2H, -CHN)	125.9
	4.77 (s, 4H, -OCH ₂ C)	64.6
	4.64 (t, J=4.72 Hz, 4H, -CH ₂ N)	51.8
	3.84 (t, J=4.74 Hz, 4H, -CH ₂ O)	70.2
	3.68 (t, J=4.99 Hz, 4H, -CH ₂ O)	70.8
	3.67 (s, 4H, -O(CH ₂) ₂ O)	71.6
	3.66 (s, 4H, -OCH ₂)	71.2
	3.60 (s, 4H, -O(CH ₂) ₂ O)	71.2

**Figure 5.** The ^1H -NMR spectra of the 1,2,3-triazole ring proton in CD_3OD for uncomplexed ligand **L2** (a) and after adding silver ion with the $\text{Ag}^+:\text{L2}$ molar ratio (b) 0.5:1, (c) 1:1 and (d) 2:1.

There are also proton shifts observed for the $\text{CH}_2\text{-N}$ as well as $\text{O-CH}_2\text{-C=C}$ groups bonded to the 1,2,3-triazole rings. The significant proton shift (0.09 and 0.14 ppm for CH_2N and $\text{O-CH}_2\text{-C=C}$, respectively) (table 2) in this region seems to confirm the additional participation of oxygen atoms in the formation of the probable sandwich-like complex. Such trends in the coordination (namely, the possible interaction of silver(I) cation with both the nitrogen atom from triazole ring and oxygen atom from the crown ether moiety) was expected on the basis of the preliminary theoretical calculations (DFT method) which indicated the possibility of such kind of cooperation is one of the energetically

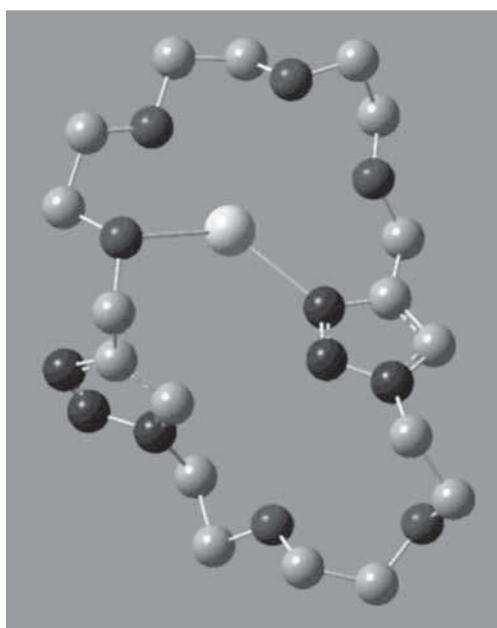


Figure 6. The model structure of calculated complex of **L2** with silver ion.

possible ways of binding in 1:1 complex, as shown in figure 6.

The existence of this form of the complex was confirmed by the ESI-MS experiments. The observed at m/z 959.70 peak (figure 7) can be attributed to the sandwich-like complex. The isotopic pattern of the signals clearly prove the suggested (existing) form of the compound.

The structure formed at the first stage of coordination process is going to reconfigure during further addition of silver ions. The significant upfield chemical shift of the $\text{O-CH}_2\text{-C=C}$ protons (from 4.77 to 4.65 ppm) suggests formation of 1:1 complex based mainly on the interactions of nitrogen atoms of triazole rings with the silver ions. Results obtained from the ESI-MS experiment (figure 7) show the characteristic (silver isotopes in double form) signal at m/z 533.34 which confirm the existence of the complex of 1:1 stoichiometry. The observed additional peaks of adducts of the parent molecule with Na^+ and K^+ ions (m/z 449.43 and 465.40, respectively) as well as the parent compound (m/z 427.37 - $\text{L2}+\text{H}^+$) suggest that in the case of **L2** the stability of the complex is much lower in comparison with the one with **L1** ligand.

In the last coordination step, dinuclear complex seems to be formed by the binding of the second silver ion with oxygen atoms from the macrocyclic ring located close to the 1,2,3-triazole unit. The lack of shift within the $-\text{O}(\text{CH}_2)_2\text{O}-$ regions suggests that the main interactions between ligand and the metal ion are situated within the triazole moieties of the ligand. Such a behavior is considerably different from that observed for the sulfur analogues as well as for similar compounds investigated in previous studies²⁶ in which other oxygen atoms were usually involved in the coordination process.

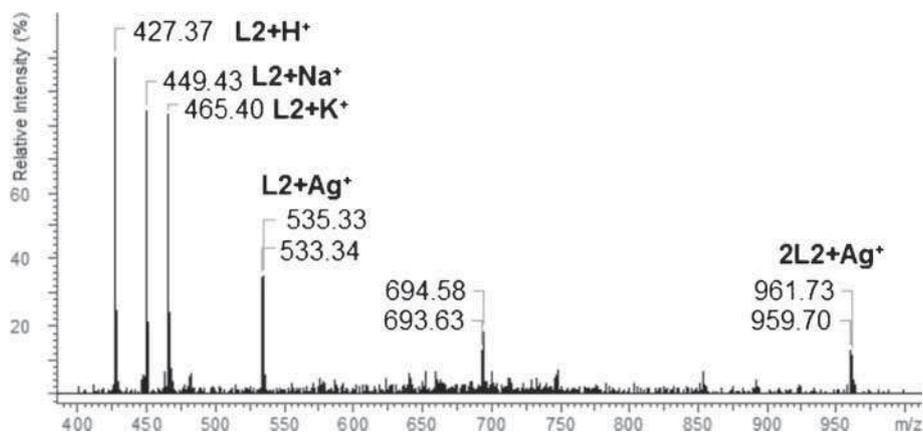


Figure 7. The ESI-MS spectrum of the complexes of **L2** with Ag^+ ions.

4. Conclusions

The diazides and dialkyne podands derived from di- or triethylene glycols were used for the preparation of sulfur and oxygen containing macrocycles with built-in 1,2,3-triazole ring. Complexation study monitored by NMR was carried out for both of the investigated ligands indicating formation of three types of complexes with stoichiometry AgL_2^+ , AgL^+ and Ag_2L^{2+} . Interestingly, in the case of ligand **L1**, the sulfur atoms of the macrocyclic system are involved in binding with silver cation in the first two stages of the complexation process. Only when the second silver ion is attached to the ligand, the nitrogen atoms of 1,2,3-triazole rings take part in the complex formation. On the other hand, in case of the ligand **L2** in the first two steps of complexation the nitrogen atoms of endocyclic 1,2,3-triazole rings are the main donors in the coordination process. The second silver ion is bound by oxygen donor atoms connected close to the 1,2,3-triazole moieties in the formation of dinuclear complex with silver ions. Such different modes of coordination in the investigated species suggest that sulfur atoms located in crown ether moiety are more favorable than nitrogen atoms in triazole rings in the binding of silver (I) cation.

Supplementary Information

All additional information pertaining to characterization of the ligands and their complexes using ^1H NMR spectra (figures S1–S8) as well as HMBC and HMQC spectra for the ligand (figures S9–S12) are given in the Supporting Information. Supplementary Information is available at www.ias.ac.in/chemsci.

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References

1. Tornøe C W, Christensen C and Meldal M 2002 *J. Org. Chem.* **67** 3057
2. Rostovtsev V V, Green L G, Fokin V V and Sharpless K B 2002 *Angew. Chem. Int. Ed.* **41** 2596
3. Lutz J-F 2007 *Angew. Chem. Int. Ed.* **46** 1018
4. Binder W H and Sachsenhofer R 2007 *Macromol. Rapid Commun.* **28** 15
5. Meldal M and Tornøe C W 2008 *Chem. Rev.* **108** 2952
6. Pasini D 2013 *Molecules* **18** 9512
7. Megiatto J D and Schuster D I 2008 *J. Am. Chem. Soc.* **130** 12872
8. Caricato M, Olmo A, Gargiulli C, Gattuso G and Pasini D 2012 *Tetrahedron* **68** 7861
9. Pacini A, Caricato M, Ferrari S, Capsoni D, Martínez de Ilarduya A, Muñoz-Guerra M and Pasini D 2012 *J. Polym. Sci. A. Polym. Chem.* **50** 4790
10. Wessjohann L A, Rivera D G and Vercillo O C 2009 *Chem. Rev.* **109** 796
11. Zhang W and Moore J S 2006 *Angew. Chem. Int. Ed.* **45** 4416
12. Gibson S E and Lecci C 2006 *Angew. Chem. Int. Ed.* **45** 1364
13. Gokel G W, Leevy W M and Weber M E 2004 *Chem. Rev.* **104** 2723
14. Szczukocki D, Dałkowski R, Krawczyk B, Zieliński M, Juszcak R, Kubisiak-Banaszkiewicz L, Olejniczak B and Andrijewski G 2015 *Arch. Environ. Prot.* **41** 15
15. Tomczyk D, Andrijewski G, Nowak L, Urbaniak P and Sroczynski D 2012 *Inorg. Chim. Acta* **390** 70
16. Tomczyk D, Nowak L, Bukowski W, Bester K, Urbaniak P, Andrijewski G and Olejniczak B 2014 *Electrochim. Acta* **121** 64
17. Brandt K, Seliger P, Grzejdziak A, Bartczak T J, Kruszyński R, Lach D and Silberring J 2001 *Inorg. Chem.* **40** 3704
18. Seliger P, Andrijewski G, Siwy M and Sęk D 2009 *Pol. J. Chem.* **83** 581
19. Seliger P, Sołtys N, Andrijewski G and Siwy M 2012 *New J. Chem.* **36** 2607
20. Romański J and Stefaniak M 2013 *Phosphorus, Sulfur Silicon Rel. Elem.* **188** 496
21. TURBOMOLEV6.0 2009, TURBOMOLE GmbH, <http://www.turbomole.com>
22. (a) Becke A D 1988 *Phys. Rev. A* **38** 3098; (b) Perdew J P 1986 *Phys. Rev. B* **33** 8822
23. Eichkorn K, Treutler O, Öhm H, Häser M and Ahlrichs R 1995 *Chem. Phys. Lett.* **242** 652
24. Stefaniak M, Jasiński M and Romański J 2013 *Synthesis* **45** 2245
25. Binauld S, Hawker C J, Fleury E and Drockenmüller E 2009 *Angew. Chem. Int. Ed.* **48** 6654; 2009 *Angew. Chem.* **121** 6782
26. Sołtys N, Seliger P, Andrijewski G and Siwy M 2013 *RSC Adv.* **3** 25351
27. Gutowska N, Pasternak B, Seliger P and Andrijewski G 2015 *New J. Chem.* **39** 1761