

RESEARCH ARTICLE

Silver Cation Coordination Study to AsW₉ Ligand – A Trilacunar Arsenotungstate Compound

Lavinia Berta, Andrei Gâz*, Francisc Boda, Augustin Curticapean

University of Medicine and Pharmacy of Tirgu Mures, Romania

Objective: The main objective of this research is to find the coordination ratio between AsW₉ and Ag⁺, as a preliminary study for synthesizing a new silver-arsenotungstate complex. **Material and method:** The ligand:cation molar ratio in complexes was determined by conductometric and potentiometric titrations of AsW₉ with silver salts: CH₃COOAg, AgNO₃. **Results:** The ratio was obtained from the inflexion points of the curves when molar ratio was plotted versus conductivity, or from the equivalence point when silver added volume was plotted versus pH value. Each graphic shows one point of inflexion corresponding to 1:1.54 ratio of AsW₉:Ag⁺. In the same manner, the equivalent volumes determined by graphical method gave the ratio 1:1.53. The spectral results confirmed that a AsW₉:Ag⁺ complex was formed since the ligand absorption maxima values have been changed from 190 nm to 197 nm in the case of using AgNO₃ and 196 nm for CH₃COOAg corresponding to the W=O_d bond, and from 246.5 nm to 274 nm (AgNO₃) and 270 nm (CH₃COO-Ag⁺) for the W-O_{b,c}-W bond. **Conclusions:** Silver cation exhibit a preference for AsW₉ in a ratio of 3 to 2. This ratio can be associated to a sandwich type arrangement, with two trilacunary Keggin building blocks incorporating 3 metal cations in a tetrahedral geometry.

Keywords: arsenotungstate ligand, silver complexes, conductometry, potentiometric titration

Received 21 April 2017 / Accepted 30 May 2017

Introduction

Polyoxometalates (POMs) represent a large family of inorganic compounds with a wide range of applications, due to their redox activity, electronic density, structural and configurational diversity [1-4].

One of the widely-used polyoxometalate-ligand is the trilacunary Keggin unit. The Na₈[HAsW₉O₃₃].17H₂O (abbreviated as AsW₉ inside the paper) used as ligand in this study, is an unsaturated arsenotungstate (which is a subclass of POMs family, with “As” as heteroatom and “W” as addenda) compound with a trilacunar Keggin structure. The electronic density of lacunae (one lacunae=six terminal oxygen) enables coordination of different metal cations [5-8].

Construction of multidimensional polyoxometalates structures using transitional metal cations as bounders have shown considerable interest in the research area over last years. New complexes combine intrinsic properties of each component as well as new properties arising from the combination of these components [9].

Among of the reported arsenotungstate complexes, the classical sandwich-type derivatives consist of two trilacunary Keggin building blocks, linked by 2 up to 6 transition metal cations at the equatorial plan [10-12].

Two different salts of the silver cation: AgNO₃, which is widely used as a precursor for many silver complexes and CH₃COO-Ag⁺ have been chosen. The silver ion is very versatile in creating supramolecular architectures due to its acceptor properties and the flexible coordination sphere. This metal ion can form from 2 up to 8 bonds with various do-

nor atoms in a wide range of coordination geometries [13].

The most important oxidation state for silver in complexes is +1. The silver ion can adopt various coordination geometries such as linear (coordination number CN=2, the characteristic geometry explained by the ion's tendency toward sd-hybridization), trigonal planar (CN=3), tetrahedral (CN=4, as in aqueous ion [Ag(H₂O)₄]⁺), octahedral (CN=6), even square antiprism (CN=8) geometry [13,14]. In POM complexes silver is generally found in tetrahedral coordinated geometry, being bounded by 2 terminal oxygen atoms from each lacunae of two different Keggin structures.

This paper is focusing on the study of AsW₉ coordination with Ag⁺ as a preliminary data for synthesizing new complexes of this arsenotungstate ligand. The synthesis of POMs proceeds by self-assembly with a large variety of structures being obtained, depending on the reaction conditions, the nature and ratio of their constitutive elements, concentration, pH or T [7,9].

Methods

Materials and apparatus

AsW₉ used in this study was synthesized as described earlier [15]. Metal cation salts (CH₃COOAg and AgNO₃) were of analytical grade from Alfa Aesar and Merck and were used without any further purification. All solutions were prepared by dissolving samples in purified water (obtained with NanoPure Diamond System (Barnstead, USA)) at a concentration of 10⁻⁵M for ligand (at a pH=7.5-8) and 2,5*10⁻²M for cations. UV spectra were recorded on an Analytik Jena SPECORD 210 spectrophotometer between λ = 190 - 400 nm in standard 1 cm quartz cuvettes. Con-

* Correspondence to: Andrei Gâz
E-mail: andrei.gaz@umftgm.ro

ductometric and potentiometric determinations were performed on an INOLAB 740 multiparameter device.

Analysis method

For every determination series, 40 mL of the ligand solution (10^{-5}M) was placed in the titration cell while the conductance and the pH of the solution was measured. Then, 4 μL $2.5 \cdot 10^{-2}\text{M}$ cation solution was added drop by drop in a stepwise manner using a calibrated micropipette. During titration conductivity and pH value were recorded after each addition. Titrations were made at $70\text{--}80^\circ\text{C}$. These values will be used in determination of ligand:cation coordination ratio. UV spectra were recorded before and after every titration to highlight modifications which occurred in each case.

Results

Results obtained by conductometry are presented in Figure 1. The graphic shows the conductivity values depending on the added titrant solution moles number.

In Figure 2 we have determined the equivalent volume for both salts by graphical method from potentiometric recorded data.

In Figure 3 we have plotted the overlaid recorded spectra of ligand and titrated solutions.

Discussions

By plotting molar ratio versus conductivity, the ligand:cation ratio was obtained from the inflexion points of the curves. In the same manner plotting pH versus added silver volume we have gathered the equivalence volume

which exhibit a 2:3 ratio between ligand and cation. These ratios are presented in Table I. From the plotted data the same ligand:cation combination ratio can be noticed for both salts type.

The structure that correspond to this ratio is an arsenotungstate common sandwich-type structure. Each trilacunar Keggin unit has 6 terminal oxygen which can coordinate metal cations. There are 2 trilacunar Keggin units, one on the top of the other, with 3 silver cations between them, where each cation bound two terminal oxygen atoms per arsenotungstate ligand unit.

The spectral analysis confirm the formation of new complexes between ligand and cation due to a shifting of the peak corresponding to $\text{W-O}_{\text{b,c}}\text{-W}$ bonds. The modified ligand absorption peak values are presented in Table II.

UV recorded spectra are characteristic to POM and show intense peak between $185\text{--}200\text{ nm}$ corresponding to W=O_{d} bonds. All spectra exhibit only the tail of this peak (Figure 3). This peak does not show large differences for W=O_{d} bond in these compounds (all having the same addenda, W). The second peak is wider and is characteristic to $\text{W-O}_{\text{b,c}}\text{-W}$ bonds (Table II). In complexes spectra, these second peaks move towards higher values of wavelength. This is due to the influence of coordinated cations especially on edges-tricentric bonds from AsW_9 structure [7, 16].

Conclusions

Silver cation exhibit a preference for AsW_9 in a ratio of 3 to 2 (from conductometry determinations) with a sandwich type arrangement. Two trilacunar Keggin building blocks incorporates 3 metal cations, each in a tetrahedral

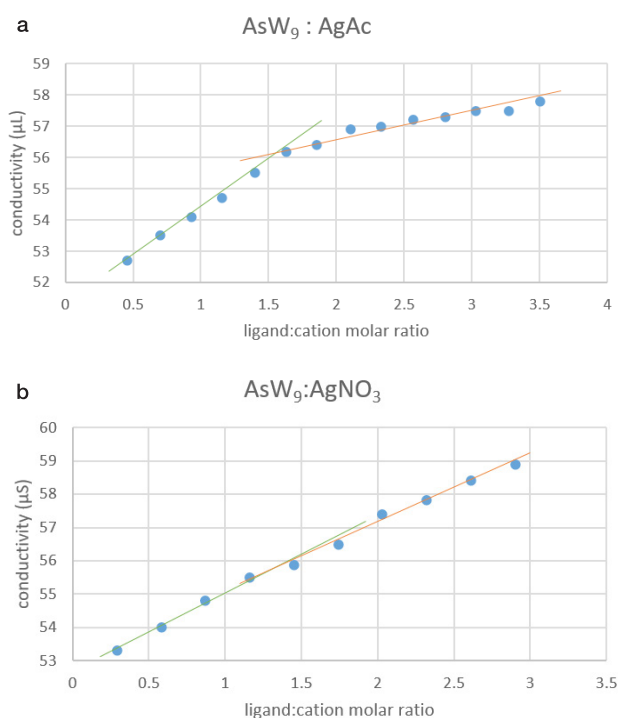


Fig. 1. Determination of inflexion point corresponding to molar ratio by conductometric titration a) $\text{CH}_3\text{COO Ag}$, b) AgNO_3

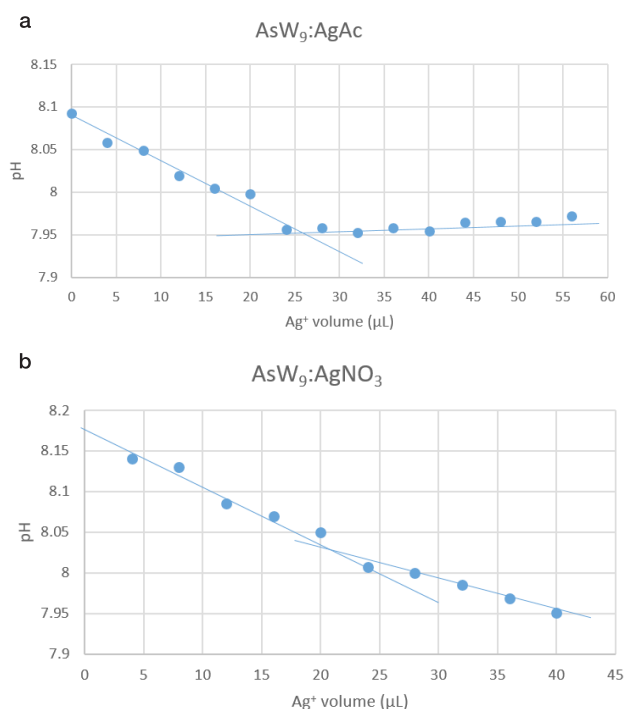


Fig. 2. Determination of equivalent volume by potentiometric titration a) $\text{CH}_3\text{COO Ag}$, b) AgNO_3

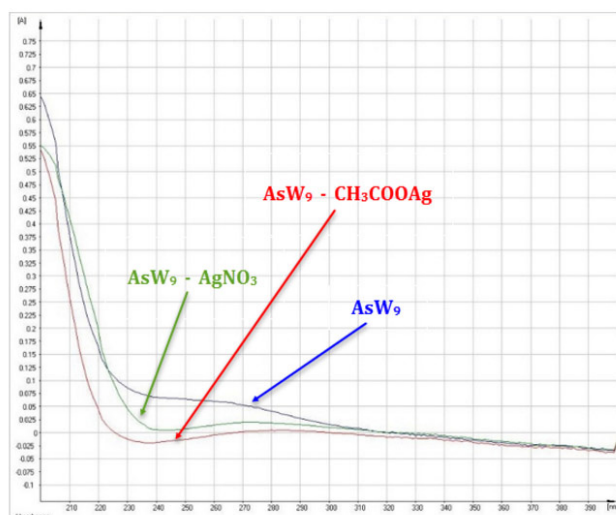


Fig. 3. The overlaid recorded spectra for all coordinative compounds and for the starting solutions of polyoxotungstate and Ag^+ solutions

Table I. $\text{AsW}_9 : \text{Ag}^+$ coordination ratio by conductometric and potentiometric titrations

| | $\text{AsW}_9 : \text{Ag}^+$ coordination ratio | |
|---------------------------|---|--------------------------|
| | Conductometric titration | Potentiometric titration |
| CH_3COOAg | 1:1.59 | 1:1.51 |
| AgNO_3 | 1:1.5 | 1:1.56 |

Table II. Absorption UV maxima values and the corresponding bonds

| | $\text{W}=\text{O}_d$ | $\text{W}-\text{O}_{b,c}-\text{W}$ |
|--|-----------------------|------------------------------------|
| AsW_9 | 190 nm | 246.5 nm |
| $\text{AsW}_9 - \text{AgNO}_3$ | 197 nm | 274 nm |
| $\text{AsW}_9 - \text{CH}_3\text{COOAg}$ | 196 nm | 280 nm |

geometry and each silver cation being bound by 2 terminal oxygen atoms from each Keggin structure. Data are confirmed by potentiometric analysis where the same ratio was noticed. These are preliminary data and further research will be performed to synthesize new arsenotungstate-silver complexes.

Acknowledgements

The research was partially supported by the UMF Tîrgu Mureş Internal Grant no. 9/23.12.2014.

Conflict of interest

None to declare.

References

- Gouzerh P, Che M – From Scheele and Berzelius to Müller, Polyoxometalates revisited and the “missing link” between the bottom up and top down approaches. *L'actualité chimique*. 2006, 298:9-22
- Chen J J, Symes M D, Fan S C et al. – High-Performance Polyoxometalate-Based Cathode Materials for Rechargeable Lithium-Ion Batteries. *Adv Mater*, 2015, 27:4649-4654
- Xing R, Wang F, Zheng A, Wang L, Fei D, Yu Y – Biological evaluation of two Keggin-type polyoxometalates containing glycine as mushroom tyrosinase inhibitors. *Biotechnol Appl Biochem*, 2015, 63:746-750
- León I E, Porro V, Astrada S, Egusquiza M G, Cabello C I, Bollati-Fogolin M & Etcheverry S B, Polyoxometalates as antitumor agents: Bioactivity of a new polyoxometalate with copper on a human osteosarcoma model. *Chem Bio Interact*, 2014, 222:87-96
- D'Souza L, Noeske M, Richards RM, Kortz U – Polyoxotungstate stabilized palladium, gold, and silver nanoclusters: A study of cluster stability, catalysis, and effects of the stabilizing anions. *J Colloid Interf Sci*. 2013, 394:157-165
- Kandasamy B, Basil BS, Haider A, Beckmann J, Chen B, Dalal NS, Kortz U – Incorporation of organotellurium(IV) in polyoxometalates. *J Organomet Chem*. 2015, 796:33-38
- Rusu D, Crăciun C – Cercetări fizico-chimice în domeniul polioxometalaților complecși. Ed. Casa Cărții de Știință, Cluj-Napoca, 2006: 45-49;40-41;73-78,239-243
- Wang Y, Zou B, Xiao LN, et al. – Two new hybrid compounds assembled from Keggin-type polyoxometalates and transition metal coordination complexes. *J Solid State Chem*. 2011, 184:557-562
- Santoni MP, Hanan GS, Hasenknopf B – Covalent multi-component system of polyoxometalates and metal complexes: toward multi-functional organic-inorganic hybrids in molecular and material sciences. *Coord Chem Rev*. 2014, 281:64-85
- Xing M, Kaifang S, Jing C, Peijun G, Hailou L, Lijuan C, Junwei Z – Synthesis, structure and electrochemical properties of a FeIII-Cell heterometallic sandwich-type tungstoantimonate with novel 2-D infinite structure $[\text{Ce}(\text{H}_2\text{O})_8][\text{Ce}(\text{H}_2\text{O})_6][\text{Fe}_4(\text{H}_2\text{O})_{10}(\text{b}-\beta\text{-SbW}_9\text{O}_{33})_2] \cdot 16\text{H}_2\text{O}$. *Inorg Chem Comm*. 2015, 60:65-70
- Bi LH, Huang RD, Peng J, Wang EB, Hu CW – Rational syntheses, characterization, crystal structure, and replacement reactions of coordinated water molecules of $[\text{As}_2\text{W}_{18}\text{M}_4(\text{H}_2\text{O})_{20}\text{O}_{68}]^{10-}$ ($\text{M} = \text{Cd}, \text{Co}, \text{Cu}, \text{Fe}, \text{Mn}, \text{Ni}$ or Zn). *J. Chem. Soc. Dalton Trans*. 2001, 121-129
- Yang W, Li H, Li Y, Chen L, Zhao J – Syntheses, structures and properties of a series of 3s-5d-4f mixed metal substituted sandwich-type arsenotungstate. *Inorg Chem Comm*. 2015, 60:71-76
- Putaj P, Lefebvre – Polyoxometalates containing late transition and noble metal atoms. *Coord Chem Rev*. 2011, 255:1642-1685
- Fox SB, Beyer MK, Bondybey VE – Coordination Chemistry of Silver Cations. *J. Am. Chem. Soc*. 2002, 124 (45):13613-13623
- Berta L, Boda F, Borodi Gheorghe et al. Two new sandwich-type compounds based on $\{\text{AsW}_9\}$ with Pd^{2+} and Pt^{4+} cations - synthesis, characterization and antibacterial activity. *Farmacia*. 2017, 65(1):63-68
- Liu J, Wang L, Yu K, Su Z, Wang C, Wang C, Zhou B – Synthesis, crystal structure and properties of sandwich type compounds based on $\{\text{AsW}_9\}$ and a hexa-nuclear unit with three supporting TM-triazole complexes. *New J Chem*. 2015, 39:1139 – 1147