Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Pankiewicz, Radosław , Schroeder, Grzegorz and Brzezinski, Bogumił(2009) 'FT-IR, semi-empirical and electrochemical studies of lasalocid ester with 2, 2'-dithiodiethanol adsorbed on silver surface', Supramolecular Chemistry, 21: 3, 202 — 206

To link to this Article: DOI: 10.1080/10610270802527010

URL: http://dx.doi.org/10.1080/10610270802527010

Supramolecular Chemistry
Vol. 21, Nos. 3–4, April–June 2009, 202–206

FT-IR, semi-empirical and electrochemical studies of lasalocid ester with 2, 2′-dithiodiethanol adsorbed on silver surface

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(*Received 2 July 2008; final version received 3 October 2008*)

A new self-assembled monolayer has been obtained on silver using a new ester of lasalocid with 2,2′-dithiodiethanol (Las11). The densely packed monolayer has been shown to remain stable and not to undergo desorption from the Ag electrode on the potential cycling. The structures of Las11 and its complex with Na^+ cations have been studied by FT-IR spectroscopic methods and the AM1d and PM5 semi-empirical methods.

Keywords: lasalocid; lasalocid ester; lasalocid ester–Na^+ complexes; FT-IR; ^1H NMR; cyclic voltammetry; AM1d calculation

1. Introduction

Ionophorous antibiotics are a group of metal cation carrier bioactive molecules and include a polyether antibiotic – lasalocid. Lasalocid (isolated from *Streptomyces lasaliensis*) is a good anticoccidial agent for cattle, sheep and chicken. In the cell membrane lasalocid exchanges metal ions against H^+, leading to changes in the pH values and to an increase in osmotic pressure inside the cell, which finally leads to the cell death (*1–7*). In our previous papers, we have reported synthesis and studies of a series of new esters of lasalocid as well as its complexes with monovalent cations by several spectroscopic and ESI-MS methods (*8–17*). Inspired by the literature data (*18–20*) and our previous work with self-assembled monolayers on silver and gold surfaces formed by bifunctional podands (*21*, *22*), we report in this paper a new type of surface modified by the lasalocid ionophore.

2. Experimental

2.1 Preparation of lasalocid ester with 2, 2′-dithiodiethanol

Lasalocid was prepared as a 1:1 complex of lasalocid with ethanol from the lasalocid sodium salt following the procedure given in Ref. (*11*).

The 1:1 complex of lasalocid-ethanol (0.01 mol) was dissolved twice in 100 cm^3 benzene. Subsequently, the solvent was evaporated. The traces of benzene were evaporated under reduced pressure. The yellow oily residue (including about 5% ethanol, NMR) was dissolved in 200 cm^3 absolute diethyl ether including 0.011 (10% excess) mole of 2,2′-dithiodiethanol (Aldrich, Sigma-Aldrich sp. z o.o., Poznań, Poland). A portion of 0.012 mol of 1,3-dicyclohexylcarbodiimide (DCC) was added to the solution and the mixture was refluxed for 10 h. The precipitated dicyclohexylurea was filtered off and the solvent was evaporated under reduced pressure at room temperature. The residue was transferred to a chromatographic column filled with silica gel (Fluka type 60). The column was first eluted with hexane to separate the traces of DCC and then with the hexane–ether (2:1) solvent mixture. The combined fractions were evaporated under reduced pressure. The yield of oily colourless lasalocid ester with 2,2′-dithiodiethanol (Aldrich; Las11), showing tendency to form a glass state, was 78%.

2.2 Preparation of complex of non-adsorbed ester

The sodium perchlorate was a commercial product of Aldrich and was used without any purification. The salt was dehydrated by several (6–10 times) evaporations from an 1:5 mixture of acetonitrile and absolute ethanol. The dehydration of the perchlorate was detected by the FT-IR spectra in acetonitrile.

The complexes of Las11 with monovalent cations were prepared by dissolving the lasalocid ester and $NaClO_4$ in equimolar amounts in acetonitrile.

CD_3CN and CH_3CN spectral-grade solvents were stored over 3 Å molecular sieves for several days. All manipulations with the substances were performed in a carefully dried and CO_2-free glove box.

2.3 Elementary analysis

The elementary analysis was carried out on Perkin-Elmer CHN 240, for the ester of lasalocid with 2,2′-dithiodiethanol

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ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610270802527010
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(Aldrich) ($C_{38}H_{62}O_9S_2$) (cald: C 62.78%, H 8.60%, S 8.82%; found: C 62.51%, H 8.55%, S 8.83%).

2.4 ^{1}H NMR measurements

The NMR spectra were recorded in CD_3CN using a Varian Gemini 300 MHz spectrometer. All spectra were locked to deuterium resonance of CD_3CN. The error in ppm values was 0.01. All ^{1}H NMR measurements were carried out at the operating frequency 300.075 MHz; flip angle, pw = 45°; spectral width, sw = 4500 Hz; acquisition time, at = 2.0 s; relaxation delay, $d_1 = 1.0$ s; $T = 293.0$ K and TMS as the internal standard. No window function or zero filling was used. Digital resolution was 0.2 Hz/point. The signals in the ^{1}H NMR spectrum of Las11 were assigned using one- or two-dimensional (COSY) spectra: δ (5) 7.20 dd; (6) 6.71 d; (8) 2.99 t; (9) ~ 2.0; (10) ~ 1.8; (11) 3.9 dd; (12) 2.92 m; (14) 2.85 m; (15) 4.08 dd; (16) 1.70 m; (17) 1.60, 1.90; (19) 3.45 dd; (20) 1.60 dt; (21) 1.50, 1.80; (23) 3.84 q; (24) 1.12 d; (25) 1.23 q; (26) 0.92 t; (27) 3.20 s; (28) 1.51 q; (29) 0.82 t; (30) 1.05 d; (31) 1.5, 1.9; (32) 0.87 t; (33) 0.88 d; (34) 3.60 s; (35) 0.89 d; (36) 2.2 s; (37) 11.2 s; (1′) 4.52 m; (2′) 2.98 m; (3′) 2.82 m; (4′) 3.59 m; (5′) 3.1 s.

2.5 Adsorption procedure

Silver strips (99.999%) were polished with alumina slurries (Buehler, Lake Bluff, IL, USA) of successively decreased final grades (down to 0.05 μm) on polishing cloths (Buehler), rinsed carefully with a dry solvent (acetonitrile or propylene carbonate). The Las11 adsorbates were formed on the silver strips from their acetonitrile solutions (0.2 M). After taking out from the liquid phase, the adsorbate was rinsed with a pure and dried acetonitrile and allowed to dry for 12 h in the water-free argon atmosphere. Furthermore, the complexation process on the surface layer was initiated by immersing the Las11 modified sample in acetonitrile $NaClO_4$ solution (0.2 M) for 4 h. After taking out from the liquid phase, the adsorbate was rinsed according to the method described previously. We proposed that in the process of adsorption, the S—S bonds were broken and the new S—Ag bonds were formed. It means that the monolayer is formed between the Ag surface and the new 2-thioethyl lasalocid ester (Las11a).

2.6 FT-IR spectroscopy

Transmission FT-IR spectra of the ester and its complex in the form of films were recorded on the same spectrometer.

The reflection–absorption spectra (RAIRS) of the adsorbates on smooth silver strips were obtained in an N_2 atmosphere on a Brucker 113V FT-IR spectrometer with an FT-80 grazing angle infrared reflection accessory and a liquid N_2 cooled TGS detector. Typically, 2048 scans with 1 cm^{-1} resolution were performed.

2.7 Raman spectroscopy

Raman spectra of the lasalocid ester were recorded on the same Brucker 113V FT-IR spectrometer with the N_2 cooled Raman detector.

2.8 Cyclic voltammograms

Potentiodynamic measurements were performed with a typical apparatus made of a potentiostat PA-20 (Elpan, Lubawa, Poland), function generator PG-20 (Elpan), X-Y recorder Endim 620.02 (VEB Schlotheim, Dresden, Germany) and a three-electrode cell comprising a silver wire (99.999%) as a working electrode, silver sheet (99.999%) as a counter electrode and a saturated calomel electrode (SCE) having a bridge filled with the electrolyte solution under the test as a reference electrode. Prior to each experiment, the working electrode was polished mechanically, as described above (see Section 2.5) and rinsed with dry propylene carbonate (PC).

Freshly prepared Ag electrodes in 0.8 M $LiClO_4$, PC solution were cycled in the potential range between 0 and −2.9 V vs. SCE, until a reproducible silver surface was attained. After the addition of Las11 into the supporting electrolyte solution, the working electrode was held at the starting potential, $E = 0$ V vs. SCE, for 1 s and at the adsorption potential, E_{ad} (between −0.2 and −1.2 V vs. SCE), for the time (t_{ad}) ranging from 30 to 360 s. Finally, the electrode potential was swept in the negative direction. In the second series of experiments, the electrochemically activated Ag electrode was removed from the 0.8 M $LiClO_4$, PC solution and immersed into the 0.2 M Las11, PC solution for 12 h. Thereafter, the electrode was rinsed with a pure solvent, allowed to dry in air conditions for 48 h and again introduced into 0.8 M $LiClO_4$, PC solution. Starting from $E = 0$ V, the electrode potential was swept in the negative direction. All measurements were performed at 298 K, while the solutions under investigation were purged with Argon (99,995).

2.9 AM1d and PM5 semi-empirical calculation

Semi-empirical calculations of the maximum surface packing density, heat of formation (HOF) and the geometric optimisation were made using the WinMopac 2002 program (*23*).

3. Results and discussion

The structure and the atom numbering of Las11 are shown in Figure 1.

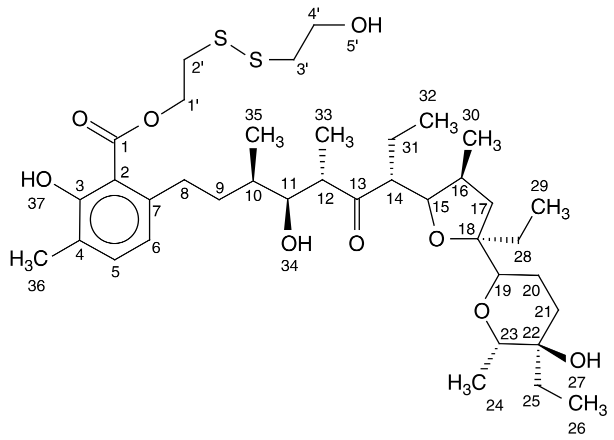

Figure 1. The structure and the numbering of the atoms of Las11.

3.1 Raman measurements

In the spectrum of Las11, there is one broad band assigned to the C—S vibration at about 670 cm^{-1} and another band at 520 cm^{-1} assigned to S—S vibration. After immobilisation, the S—S band disappears. This observation demonstrates that the S—S bond after immobilisation is broken and suggests that a new Ag—S bond has been formed.

3.2 FT-IR measurements

The FT-IR spectra (Figure 2) of the Las11 and its 1:1 complex with Na$^+$ cations, in the form of films obtained by the absorption technique, and the RAIRS spectra of the adsorbed Las11a and its 1:1 complex with Na$^+$ cation on the silver surface, are compared. The same spectra in the ranges of the ν(C═O) vibrations are shown on an extended scale in Figure 2(b). A comparison of these spectra demonstrates that the adsorption of the Las11 molecule has no influence on the spectral features. The same is true for the respective spectra of the Las11–Na$^+$ complexes. The main result is, however, the evidence that the Las11a molecules have been adsorbed on the silver surface and can also complex Na$^+$ cations.

With the complexation process of Na$^+$ cations by Las11 molecules both in films and as adsorbed species, the band assigned to the O—H stretching vibration of the hydroxyl groups shifts towards higher wavenumbers (from 3400 towards 3500 cm^{-1}), indicating that these hydroxyl groups are in the complex weaker hydrogen bonded than in the free Las11 molecule. This also means that with the complex formation, the structure of the ester strongly changes.

In the spectrum of Las11 in the range of the stretching vibration of C═O bonds, there is one band at 1715 cm^{-1} assigned to the ketone group and one band at 1657 cm^{-1} assigned to stretching vibration of C═O ester group. In the spectra of the 1:1 complexes of Las11 with Na$^+$ cations, compared with the spectra of Las11, the first band is shifted toward lower wavenumbers and arises at 1705 cm^{-1} and the position of the second one is almost unchanged. This observation demonstrates that the ketone group is involved in the complexation process, whereas the

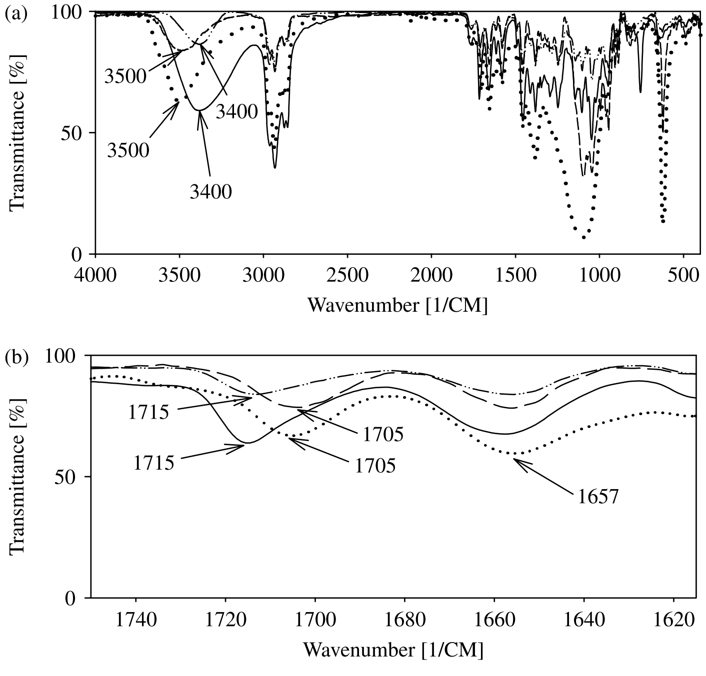

Figure 2. The FT-IR spectra (film) of (–) Las11 and its (·) 1:1 complexes with Na$^+$ and the ATR spectra of (–··–) Las11 adsorbed on a silver surface and its (– –) complexes with Na$^+$ cations (a) 4000–400 cm^{-1}. The same spectra in the extended scale (b) 1750–1615 cm^{-1}.

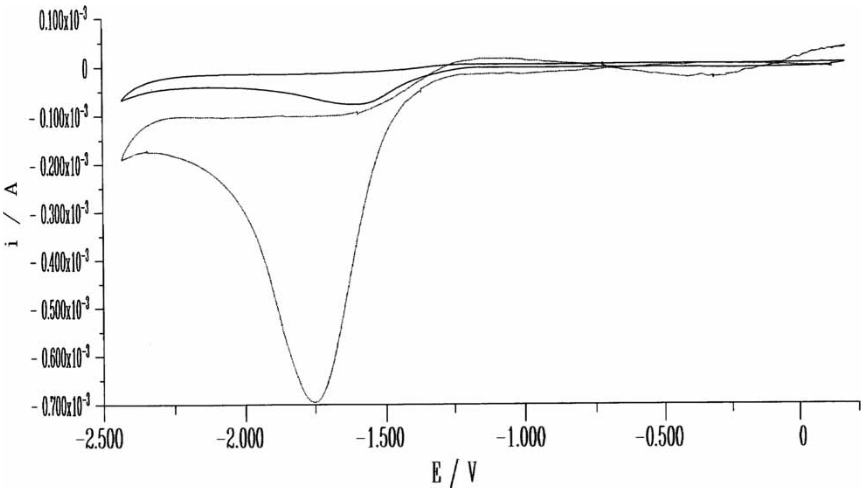

Figure 3. Cyclic voltammograms for Ag electrode in 0.8 M $LiClO_4$ + PC (–) and 0.8 M $LiClO_4$ + PC + 0.2 M Las11 (---). Scan rate 0.05 V/s.

ester group is not engaged in this process. The last result is understandable because the ester group of Las11 is hydrogen bonded via intramolecular hydrogen bond with the hydroxyl group in the *orto*-position of the salicylic part. Analogous results were obtained for other monovalent cations such as lithium or potassium.

3.3 Potentiodynamic measurements

Self-assembled monolayer (SAM) was studied for lithium cations by cyclic voltametry. Figure 3 depicts two cyclic voltammograms in the supporting electrolyte (0.8 M $LiClO_4$ in PC) and in solution containing 0.2 M Las11. The addition of Las11 modifies the cyclic voltammogram not only by increasing the current at negative potentials due to electroreduction of PC and Li deposition but also by exhibition of the adsorption–desorption wave at ca. − 1.15 V. The detection of such a wave indicates the adsorption of Las11 species at the silver electrode.

3.4 PM5 and AM1d calculations

The heats of formation, calculated by the PM5 method, of the Las11 molecule and its complexed and uncomplexed species with Na^+ cations are collected in Table 1. These data show that the formation of the 1:1 complex is energetically favoured. The calculated structure of the complex, shown in Figure 4, reveals two parts of the molecule: one part includes the salicylic group stabilised by one intramolecular hydrogen bond, while the rest of the molecule is stabilised by the interactions of six oxygen atoms with the monovalent cation. This situation is comparable to that in the previously studied lasalocid esters (*8–17*).

Table 1. Heat of formation (HOF, kJ/mol) of Las11 and its complexes with Na^+ cations calculated by PM5 method.

	HOF (kJ/mol)	ΔHOF
Las11	− 1947.20	–
Las11:Na^+ (complexed)	− 1706.09	− 353.28
Las11 + Na^+ (uncomplexed)	− 1352.81	
Las11:2Na^+ (complexed)	− 874.58	− 116.16
Las11 + 2Na^+ (uncomplexed)	− 758.42	

ΔHOF = $HOF_{(complexed)} - HOF_{(uncomplexed)}$.

Figure 5 presents the structure of Las11–Na^+ complex adsorbed on the silver surface calculated by the AM1d method. As follows from the calculations, the area per one adsorbed molecule in a densely packed layer is 0.93 nm^2, which means the surface concentration of 1.08 × 10^{14} molecules per cm^2 at the saturation coverage of the silver surface. A single lasalocid ester molecule covers a relatively larger area, in comparison with the other

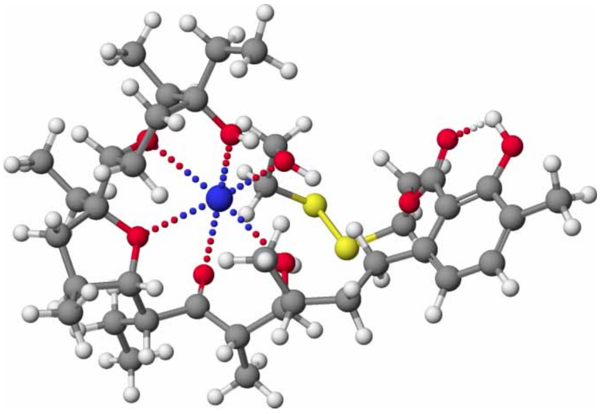

Figure 4. Calculated structure of the Las11 complex with Na^+ cation.

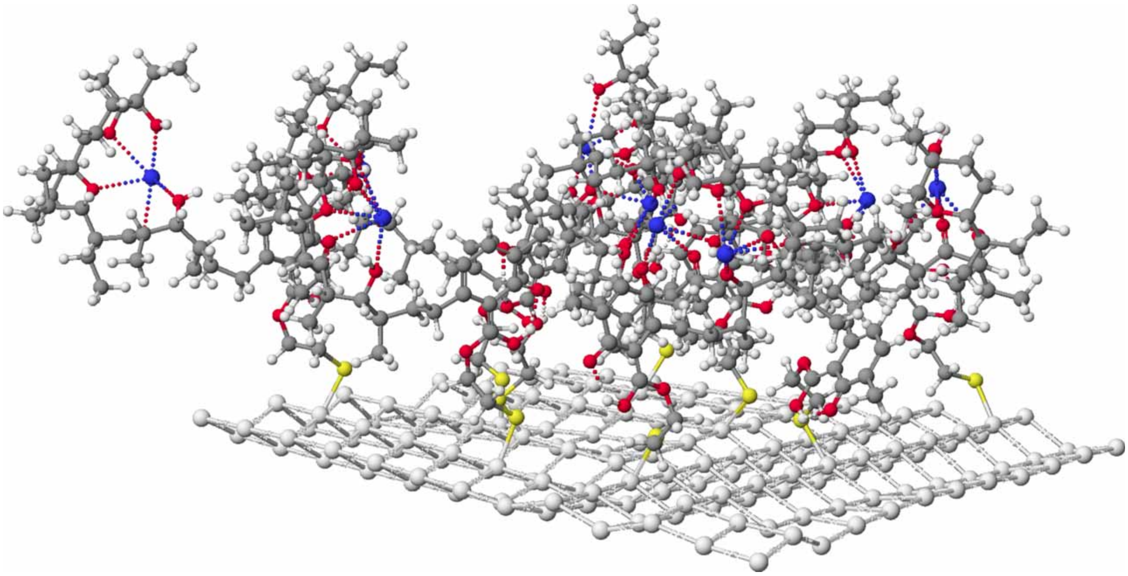

Figure 5. Calculated structure of the surface layer with 60% of the maximum packing density of Las11 molecules on Ag with Na^+ cations.

molecules studied (*21*, *22*), because of its pseudo-ring spatial structure.

4. Conclusions

The RAIRS, Raman spectra and potentiodynamic measurements have indicated a strong chemisorption of lasalocid ester on silver surface. The FT-IR study has shown that the adsorption of the Las11 molecule has no influence on its complexation ability.

Acknowledgements

This paper was financially supported by the Polish Ministry of Science and Higher Education.

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