Short communication

Study of the Complexation of 1,3-diethyl 2-(azulen-1-ylmethylene)propanedioate with Lanthanide Cations

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Received: 03-02-2014

Abstract

This work is devoted to the electrochemical characterization of 1,3-diethyl 2-(azulen-1-ylmethylene)propanedioate by cyclic voltammetry and differential pulse voltammetry. The redox processes are established, analyzed and assessed to the particular functional groups at which they take place. The complexation behavior towards lanthanide metal ions (Sm^{3+}, Eu^{3+}, Yb^{3+}, Tb^{3+}) was studied by electrochemical methods and UV-Vis spectroscopy.

Keywords: Ligands, azulene, cyclic voltammetry, differential pulse voltammetry, UV-Vis spectroscopy, lanthanide cations

1. Introduction

Azulenes are organic compounds characterized by a five-membered cyclic moiety which is electron rich and a seven-membered cyclic moiety which is electron poor. This dual "push-pull" structure where the azulenyl is the electron donating group and the substituent is the accepting group provides some interesting properties to the molecule.[1] Due to this particular structure azulenes can be involved in both oxidation and reduction processes and the nature of the substituent and its orientation greatly influences the electrochemical properties (number of redox waves and potentials).[2]

Azulene derivatives are also versatile starting materials and the formation of polymers has been widely reported.[3–5] Furthermore, there are many papers now that describe the properties of azulene polymers formed by electrochemistry, which have very similar characteristics to the azulene polymers chemically synthesized. In the past years, a considerable number of studies have been made on the preparation of polyazulene films,[4] or on metal complexes of azulene derivatives.[5]

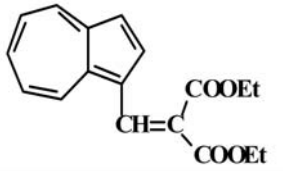
Similar compounds containing other electron donor moieties such as ferrocene,[6] p-dimethylaminophenyl,[7] fullerenyl[8] and electron rich groups, like crown ethers[9] or amides,[10] have been already investigated as sensors for metal ions,[11,12] and particularly as sensors for lanthanide ions. In the last decades, lanthanides have contributed to a range of modern materials leading to increasing interests in fundamental research and technological applications from environmental and energy to biological sciences.[13–16]

To our knowledge, there is no literature data regarding lanthanide ions complexation using ligands based on azulene. This paper aims to bring new information on the complexation ability of a new azulene derivative 1,3-diethyl 2-(azulen-1-ylmethylene)propanedioate (**1**) and the complexation properties towards Samarium (Sm^{3+}), Terbium (Tb^{3+}), Ytterbium (Yb^{3+}) and Europium (Eu^{3+}) lanthanide metal ions.

2. Experimental Section

The starting materials used for the preparation of compound **1** were purchased from Aldrich and used wit-

hout further purification. Acetonitrile and tetrabutylammonium perchlorate (TBAP) from Fluka were used as received for solvent and supporting electrolyte. The azulene derivative **1** with the structure given bellow was synthesized by condensation of 1-azulenecarbaldehyde with diethyl malonate in the presence of catalysts and it was characterized by elemental and spectral (^{1}H-NMR, ^{13}C-NMR, UV-Vis) analysis.[2a,17–19]



The lanthanide electrochemical recognition with this type of ligand was performed in acetonitrile (CH_3CN) solutions containing 0.1M TBAP. In the present work we present the results for Yb^{3+}, Tb^{3+}, Sm^{3+}, Eu^{3+} cations which were used as trifluoromethanesulfonate (triflate) salts (from Merck).

The electrochemical experiments were carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using a PGSTAT12 AUTOLAB potentiostat coupled to a three-compartment cell. The CV curves were recorded at scanning rates between 0.1 – 1V/s. DPV curves were recorded at 0.01V/s with a pulse height of 0.025V and a step time of 0.2 s. The working electrode was a glassy carbon disk (3 mm in diameter). The active surface was polished before each determination with diamond paste (200 μm). Ag/10 mM $AgNO_3$ in 0.1 M TBAP, CH_3CN was used as the reference electrode. The potential was referred to the potential of the ferrocene/ferricinium redox couple (Fc/Fc^+) which in our experimental conditions was +0.07 V. A platinum wire was used as the auxiliary electrode. The determinations were performed at 25 °C under argon atmosphere.

The spectral study was performed using a JASCO V-670 spectrophotometer, in a cuvette with an optical path of 10 mm.

3. Results and Discussion

3. 1. Electrochemical Study of Compound 1

The electrochemical experiments were carried out by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Anodic and cathodic curves were recorded individually, starting from the open circuit potential. CV and DPV curves were recorded for various concentrations (0–3.5 mM) of the studied compound in solutions of 0.1M tetrabuthylammonium perchlorate (TBAP) in acetonitrile (CH_3CN). The data provided by the cyclic voltammetry experiments allowed the establishment of the reversible (r), quasireversible (q) and irreversible (i) character of each peak.

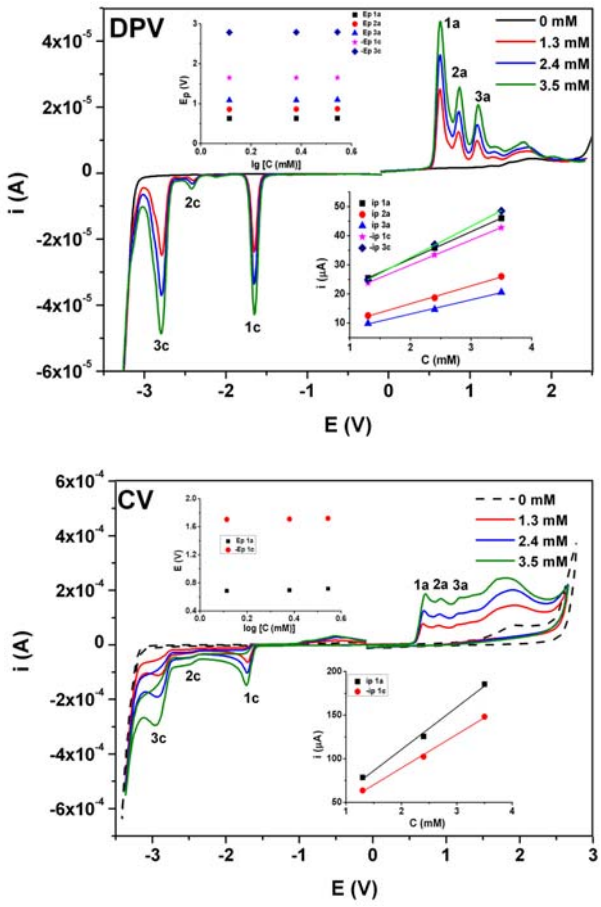


Figure 1. DPV and CV (0.1 V/s) curves for different concentrations of **1** in 0.1M TBAP, CH_3CN; Insets: linear dependences of peak potentials and peak currents respectively, on **1** concentration from DPV and CV curves

The DPV curves obtained for different concentrations of 1 are presented in Fig. 1. Four anodic (1a–4a) and three cathodic (1c–3c) processes are observed, denoted in the order in which they appear in the voltammograms. The CV curves for increasing concentrations of 1 are shown in Fig. 1.

The influences of the scan domain and the scan rate upon the CV curves are presented in Fig. 2. Starting from the information given by Figs. 1 and 2 the character of each peak was assessed (Table 1). The reversible (r), quasi-reversible (q) or irreversible (i) character of the processes was estimated by taking into account the presence of a counter peak in the reverse scan; for example for peak 3c there is a response peak 3c' in the reverse scan situated at a potential shifted with less than 60 mV in respect to 3c. This behavior allowed the evaluation of 3c as a quasi-reversible process. In the case of 1c, 2c, 1a–4a there is no response peaks in the reverse scans; these peaks were qualified as due to irreversible processes.

In Scheme 1 are represented only the first oxidation and reduction processes of the ligand (corresponding to processes 1a and 1c, respectively, from Table 1). Peak 2c

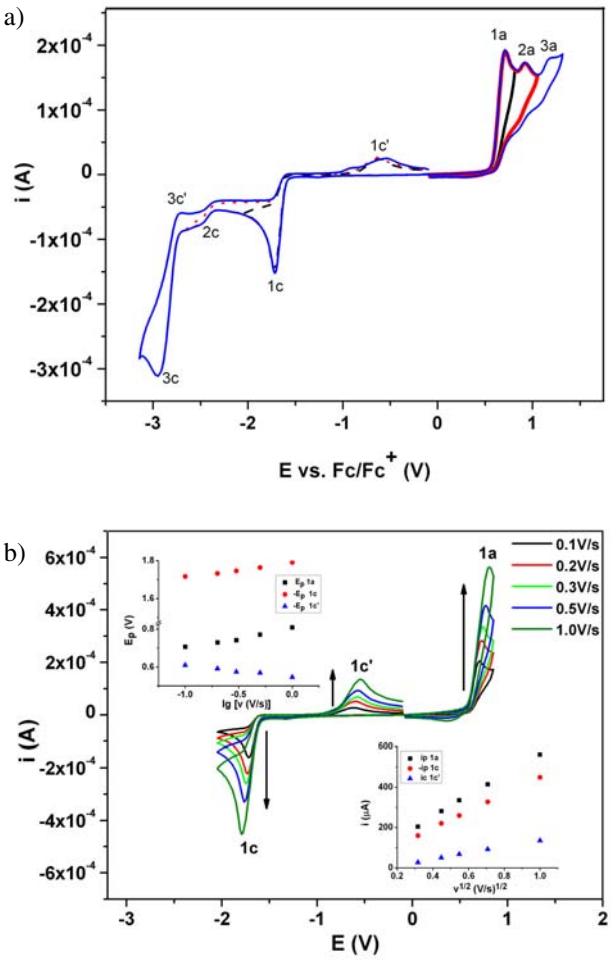


Figure 2. CV curves for various scan domains at 0.1V/s (a) and at different scan rates in the domains of the peaks 1c and 1a, respectively, (b) for **1** (3.5 mM) in 0.1M TBAP, CH_3CN

presumably representing the reduction of azulene dianion dimer 3-3 ' has a very low intensity (see Fig. 1), which shows a relatively high stability of the radical anion with a weak tendency to di(poly)merization. 3c represents the reduction peak which discriminates the polyene system of the azulene. Peak 2a is of a higher intensity than 2c which indicates a lower stability of the azulene radical cation compared to the corresponding radical anion, due to the presence of the vinylmalonic electron withdrawing substituent. The radical cation forms oligomeric species that oxidize immediately after their formation.

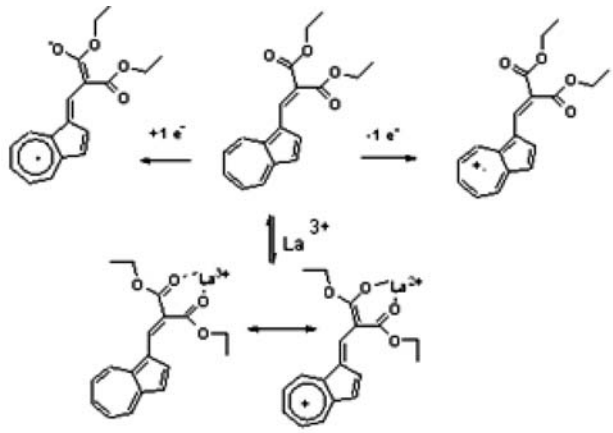
The presence of multiple peaks in a low range of potential makes very difficult the localization of positive charges on certain elements of the vinylazulene structure, but it is clear that this vinylazulene system is responsible for the loss of electrons at the anode, finally leading to the formation of polyoxygenated by-products due to the presence of traces of water in the electrolyte.

Except peaks 1c and 1a, the other peaks represent non-unitary processes and therefore they were not listed in Scheme 1.

Table 1. Peak potentials (V) of the peaks and their assessment for **1**

Peak no. / Technique	DPV	CV	Assessed process
1c	–1.652	–1.725 (i)*	Radical anion formation
2c	–2.420	–2.530 (i)	Reduction of the oligomeric intermediate
3c	–2.813	–2.964(q)*	Azulene reduction
1a	0.645	0.710 (i)	Radical anion formation
2a	0.864	0.929 (i)	Oligomer oxidation
3a	1.103	1.189 (i)	Oligomer oxidation
4a	1.668	1.811 (i)	

*q – quasi-reversible process; i – irreversible process.



Sheme 1

3. 2. Electrochemical Complexation Experiments

Complexation tests were performed in organic media (0.1M TBAP in CH_3CN). The CV curves for the reduction of lanthanide metal ions were recorded. The results obtained for Sm^{3+} are presented in Fig. 3. They

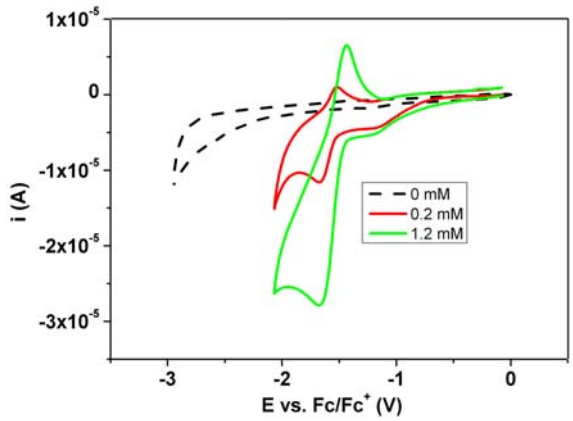


Figure 3. Cyclic voltammetry curves in 0.1M TBAP, CH_3CN on a glassy carbon electrode (3 mm in diameter) in the presence of increasing amounts of $Sm(OTf)_3$

show a couple of peaks corresponding to the reversible reduction of Sm^{3+} to Sm^{2+} at –1.57 V. This value corresponds to what was reported for Sm^{3+} reduction in other solvents.[20] This potential is almost identical with the one for the ligand reduction and therefore the cations' reduction could not be observed individually if there is no interaction between these species. However, several new peaks are observed by mixing samarium triflate with compound **1**. The peaks observed in the DPV experiment are shown in fig 4.

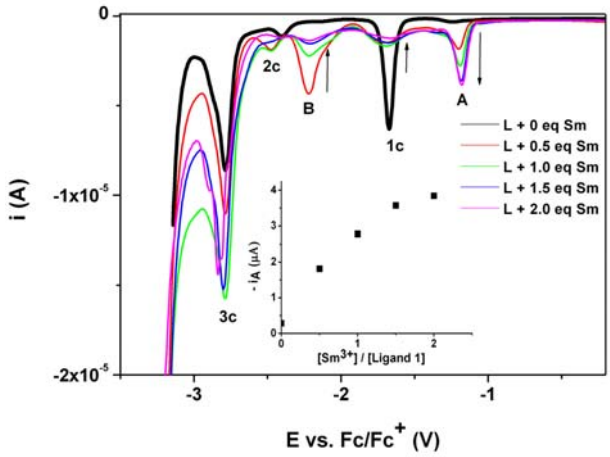


Fig. 4. DPV cathodic curves in 0.1M TBAP, CH_3CN on a glassy carbon electrode (Φ = 3 mm) in a solution of **1** (5×10^{-4} mol / L) in the absence (bold black line) and in the presence of increasing amounts of $Sm(OTf)_3$ (0.5, 1, 1.5, 2 equivalents)

The CV and DPV curves in anodic and cathodic scans were recorded in a solution of ligand **1** in the presence of increasing amounts of Sm^{3+} ions. The first oxidation potential of the ligand is not significantly influenced by the presence of samarium trivalent ions, which could be an indication that the azulene moiety is farther from the complexation site (azulene moiety is the most oxidizable part of the molecule), as shown in the proposed mechanism (Scheme 1).

On the contrary, the cathodic part of the voltamogramm is deeply influenced by the presence of Sm^{3+} showing a complexing interaction between Sm^{3+} and the carboxylate groups of the malonic fragment of **1** (Scheme 1).

The addition of the Sm^{3+} salt to a solution of **1** leads to the formation of a complex which reduces at peak A. This peak is situated at a potential which is lower (–1.17 V) than the first reduction peak of the ligand **1** (1c). This is due to its three positive charges, situated mainly on the metal but also on the azulene moiety as shown by the limiting structures of the complex (Scheme 1). However, the rest of the ligand which remained un-complexed in the solution is reduced at a higher potential, B (–2.24 V), due to the shielding effect of the Sm^{2+}–**1** complex adsorbed on the electrode. The latter complex is discharged only at a much higher negative potential, 3c (–2.79 V). Peak B decreases in intensity as new quantities of Sm^{3+} triflate are added, forcing the free ligand complexation.

All the cations were investigated by electrochemistry and the obtained results were similar. The fine differences put in evidence between the electrochemical behaviour of each cation during the complexation event cannot be rationalized for the moment. More investigations are necessary and the work is in progress.

3. 3. Spectral Complexation Experiments

In order to establish the influence of each lanthanide ion upon the UV-Vis spectrum successive additions of the lanthanide triflate concentrated stock solution have been realized. The obtained spectra were analyzed in different concentration domains, expressed as number of equivalents (eq) of lanthanide ions. Each domain of adding (0–5 eq; 0–25 eq; 0–125 eq and further) was examined. It was concluded that changes appeared only after a higher number of equivalents than expected for a stoichiometric complexation was added. Figure 5 presents the UV-Vis spectra obtained during the addition of $(CF_3SO_3)_3Yb$ and the evolution of the peak absorbance with the number of Yb^{3+} equivalents.

It appears from this first domain of addings that the changes due to the continuous adding of the cation solution vary linearly untill 20 eq. and that they tend to a limiting value. Therefore a higher number of lanthanide equivalents were further added after and the spectra were recorded. The results shown in Figure 5 (0–250 eq.) evidenced this behavior. The peak continuously increases untill about 100 equivalents and then it decreases.

The absorbance bands of the azulen-1-yl-vinyl ester **1** diminish and a new peak appears during the lanthanide adding. This new peak was attributed to the complex formed between the ligand **1** and the Yb^{3+} cation.

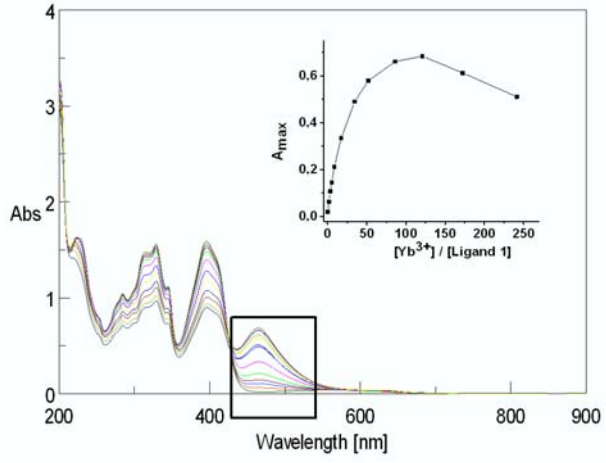


Figure 5. Variation of the absorbance at λ = 465 nm with the number of Yb^{3+}equivalents added. Inset: UV-Vis spectra in solutions of **1** (0.058 mM).

3. 4. Comparison Between Complexations with Lanthanide Cations

The spectral study was similarly performed for Tb^{3+}, Sm^{3+}, and Eu^{3+} cations (added as triflates). The results are given in Fig. 6 A and B for different domains of adding. Table 2 gives the maximum values of the wavelength for the new peaks and their equations in the case of each lanthanide cation.

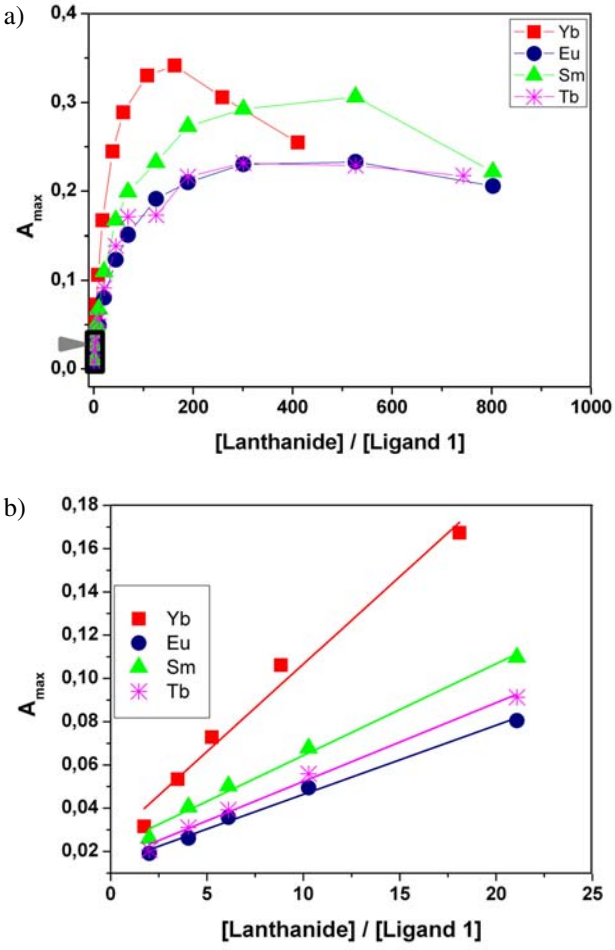


Figure 6. Variation of the complexes' absorbances at the maximum wavelength (Table 2) with the number of added lanthanide equivalents (**A**); Detail of the linear parts of A (**B**)

The Figures above shows that the absorbance of the new peak (obtained after addition of lanthanide cations in solution of **1**) increases linearly until approximately 20 equivalents, then it tends to reach a maximum value. This behavior could be due to the formation of dipole-dipole bonds between the ligand and the investigated cations. The obtained slopes vary in the order Yb>Sm>Tb>Eu. The linear behaviour of A_{max} = f([Lanthanide] / [Ligand **1**] ratio) is seen for each of the investigated cations for almost the same domain (till around 20 equivalents).

The chromophores of the new visible band of the complexes have very close values (Table 2).

Table 2. λ_{max}, A_{max} and R^2 for the corresponding complexation peak of **1** (0.058 mM) with lanthanide cations

Cation	λ_{max} (nm)	A_{max}* (10 eq.)	Equation of the linear domain of A_{max} (correlation coefficient, R^2)
Yb^{3+}	465	0.106	y = 0.026 + 0.0081 × x (0.977)
Tb^{3+}	464	0.052	y = 0.016 + 0.0036 × x (0.993)
Eu^{3+}	464	0.046	y = 0.014 + 0.0032 × x (0.992)
Sm^{3+}	463	0.064	y = 0.022 + 0.0042 × x (0.989)

*measured for 10 eq. of lanthanide ions

4. Conclusions

A study of the complexation of the azulenic ligand, 1,3-diethyl 2-(azulen-1-ylmethylene)propanedioate, with some lanthanide cations (Yb^{3+}, Tb^{3+}, Sm^{3+} and Eu^{3+}) was performed by electrochemical and spectral methods. The characteristic redox properties for this azulen-1-yl-vinyl ester were influenced by the addition of the lanthanide cations. The formation of new peaks corresponding to complexed species was observed both by electrochemistry and spectral analysis. Furthermore, a linearity domain was observed for each cation complexation until 20 equivalents added. This stands for a slow stoichiometric complexation. The intensity of the absorbance of the lanthanide complexes were found to be similar being maximum for Yb^{3+} complex. The fine differences put in evidence between the behaviour of each cation during the complexation event are still investigated.

5. Acknowledgements

The authors are grateful for the financial support from UEFISCDI project ID 15/2011 and European Social Found through POSDRU/159/1.5/S/137390 project.

6. References

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Povzetek

Z uporabo ciklične voltametrije in diferenčne pulzne voltametrije smo ovrednotili 1,3-dietil 2-(azulen-1-ilmetilen)propandioat. Proučevali smo redoks procese, ki potekajo na določenih funkcionalnih skupinah. Komplekse z lantanidnimi kovinskimi ioni (Sm^{3+}, Eu^{3+}, Yb^{3+}, Tb^{3+}) smo raziskovali z elektrokemijskimi metodami in UV-Vis spektroskopijo.