

Electrochemical Study of the Lanthanides Coordination with Pyridine Heterocycles

ROMPHYSICHEM16- Section 4: Electrochemistry. Corrosion. Ionic liquids



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Introduction and objectives

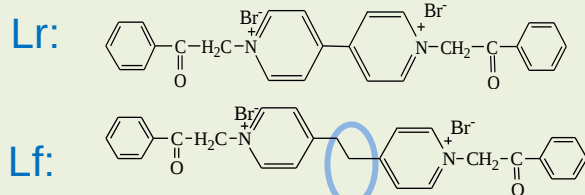
- Antitumor potential of lanthanide underpins recent research for obtaining new molecules used in cancer diagnosis and therapy. Lanthanides promote cell proliferation and induce apoptosis. Thus, the new compounds were investigated as inhibitors, cytotoxic agents, radiation therapy and photodynamic therapy as biosensors.
- It proposes a study of electrochemical evaluation of newly synthesized complexes (Ln-cycles pyridine) to identify electron transfer reactions in anticipation of their behavior in cancer diagnosis or clinical treatments.

Materials and methods

- Quaternary pyridinium salts derived from 4,4'-bipyridinium (**Lr**) and 1,2-bis-(4-pyridinium)ethane (**Lf**), lanthanum (III) and neodymium (III) sulfate in methanol (**Met**), triethylamine (**Et₃N**), dimethyl sulfoxide (**DMSO**)
- Studies of cyclic voltammetry (**CV**-Bio-logic SP 150) to predict their behaviour in medical applications (**CV**)
- Spectrophotometric (UV-Vis) and conductometric measurements

Results

Synthesis of lanthanide complexes

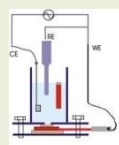


La: **Lr(Lf):Et₃N:Met**

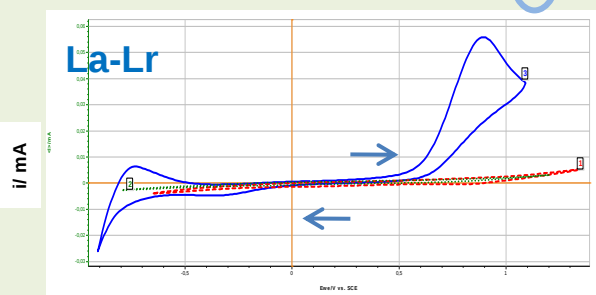
Nd: **Lr(Lf):Et₃N:2Met**

Electrochemical Study(CV)

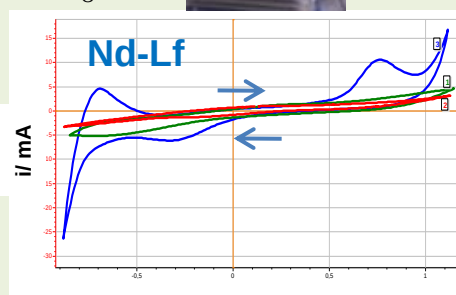
Bio-logic SP 150



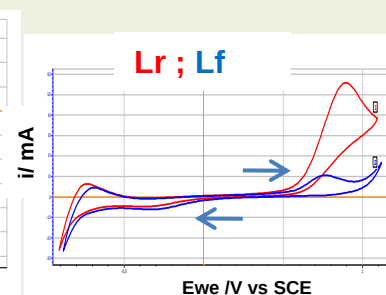
1.m.aqueous
2.m.alcoholic
3.m. aprotic
(DMSO)



Ewe IV vs SCE



Ewe IV vs SCE

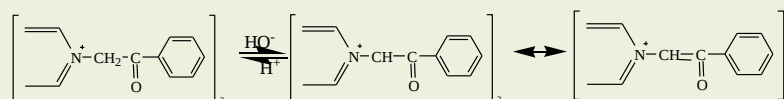


Ewe IV vs SCE

CE: Pt(wire)
WE: Pt
RE: Saturated Calomel E = +0,242 V

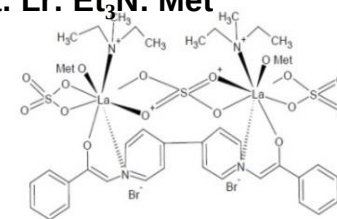
DMSO	Epa1 mV	Epc mV	ΔEp/2 mV	Epa2 mV	E° mV	Ip1 μA	Ip2 μA
La-L1	-746	-373	186,5	886	443	6,14	55,60
Nd-L2	-690	-313	188,5	761	380	4,51	10,53

Electron transfer mechanism

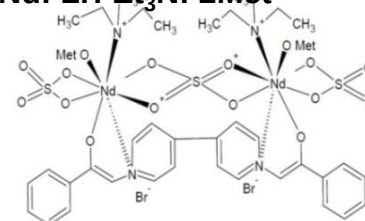


Proposed Structures of lanthanide complexes

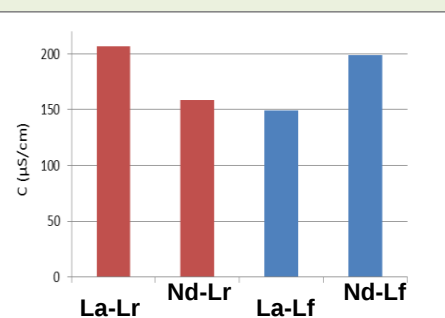
La: Lr: Et₃N: Met



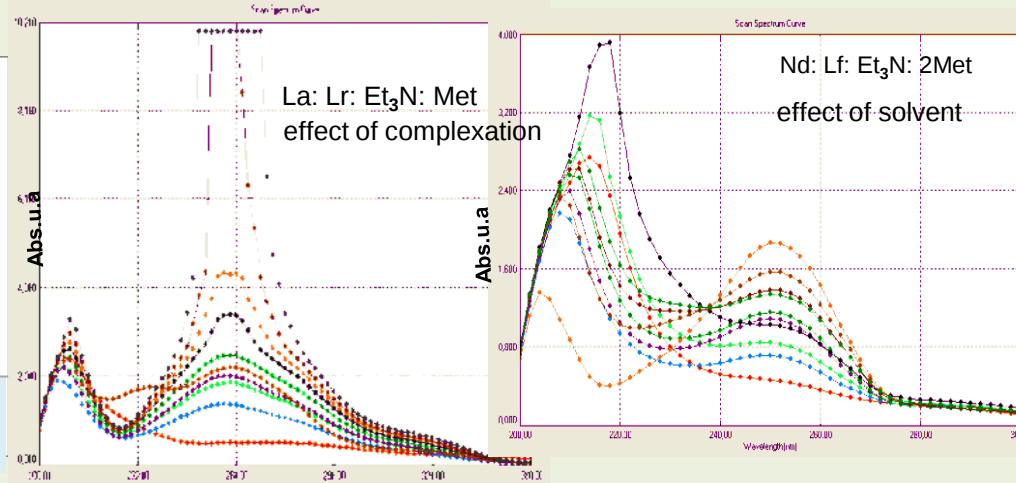
Nd: Lr: Et₃N: 2Met



Conductometry (Consort C862)



UV-Vis of lanthanide complexes (0,1mM)



Conclusion

- Cyclic voltammograms registered show changes in the redox potential of the complexes compared to the free N-heterocyclic ligands and this behavior is dependent on the pH, the potential and the scan rates applied.
- The voltammograms in aprotic solution (DMSO) indicates enhanced electronic transfer processes of one/two electrons compared to the aqueous or alcoholic medium. Ethylene group from the N,N'-bis (p-bromophenacyl)-1,2-bis(4-pyridyl)-ethane dibromide induces changes in the electrochemical performance in comparison with the ligand N,N'-bis(p-bromophenacyl)-4,4'-bipyridinium dibromide and determines preferential arrangements in complexes.
- The electrochemical properties indicate and recommend novelty compounds in biomedical applications.

References

J. O'M. Bockris, A. K. N. Reddy, M. Gamboa-Aldeco, *Modern Electrochemistry. Fundamentals of Electrochemistry*, Vol 2A, cap.6, Kluwer Academic/ Plenum Publishers, New York, 2000
M. Bond, *Broadening Electrochemical Horizons. Principles and Illustration of Voltammetric and Related Techniques*, Oxford University Press Inc., New York, 2002.
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