

Synthesis, structural elucidation, electrochemical and UV/Visible absorption studies of pyridyl-carotenoid ligands to rhenium (I) and platinum (II).

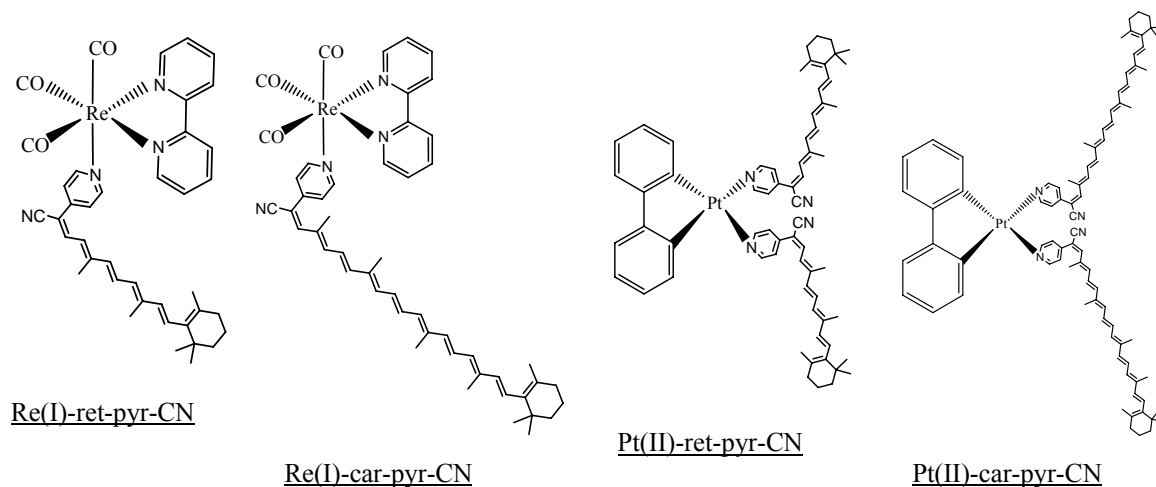
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Abstract. Condensation of all-trans-retinal and β -apo-8'-carotenal with 4-pyridyl acetonitrile monohydrochloride were performed. UV-Visible absorption data in acetonitrile of the condensed ligands show a bathochromic shift in its $\pi \rightarrow \pi^*$ transition observed at $\lambda_{\text{max}} = 446$ and 502 nm from 380 and 458 nm respectively. X-ray data for the pyridyl-retinal ligand showed space group symmetry of $P2_1/n$. Metal complexes of these ligands were further synthesized. Mass spectrometric analysis for the rhenium (I) complexes showed molecular ion peaks at m/z (ESI) = 811 for the retinal while the carotenal is observed at m/z (FAB) = 943. UV-Visible absorption data of the rhenium (I) complex showed solvatochromic behavior. The λ_{max} of the short-chain was red shifted to 464 nm in acetonitrile and 511 nm in methylene chloride. The λ_{max} of the long-chain was observed at 522 nm in acetonitrile and 612 nm in methylene chloride. UV-Visible absorption data of the platinum (II) complex of the short-chain also showed solvatochromism. It was observed at 458 nm in acetonitrile and 481 nm in dichloromethane. The λ_{max} of the long-chain was observed only at 542 nm in dichloromethane. Cyclic voltammetry showed irreversible oxidation peaks for all ligands and metal complexes.

1. Introduction

Inorganic photosensitizers are used in Gratzel cells as light-harvesters and electron pump¹. Analogs of the known $[\text{Ru}(\text{bpy})_3]^{2+}$ have been synthesized² to enhance its efficiency to convert solar energy into electrical energy. Complexes involving Re, Pt and Cu are also popular in this field³. In this study, derivatives of naturally occurring carotenoids have been synthesized and characterized due to their better light-harvesting properties in photosystems vital to plant photosynthesis⁴. These derivatives were then coordinated to rhenium (I) and platinum (II). The structures are given below:



2. Experiment, Results and Discussion

Condensation of all-trans-retinal and β -apo-8'-carotenal with 4-pyridyl acetonitrile monohydrochloride were performed via acid-catalyzed Knoevenagel Condensation⁵ in benzene under Ar conditions. Compounds retinal-pyridine-cyano and carotenal-pyridine-cyano were both isolated in a column (stationary phase: alumina; mobile phase: 7:1 (v/v) methylene chloride/chloroform. Figure 1 shows the x-ray structure of retinal-pyridine-cyano compound having a P2₁/n space group. Tables 1 and 2 shows UV-Visible and Mass spectral data. Solvatochromism is observed for Re(I) and Pt(II) short-chained derivatives. Electrochemical Data showed irreversible oxidation peaks indicating good electron transfer in the system. Figure 3 shows cyclic voltammogram of Re(I)-car-pyr-CN.

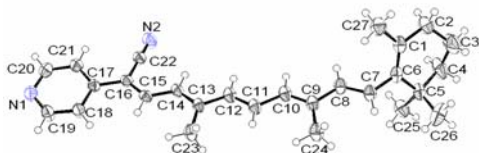


Fig. 1. X-ray structure of retinal-pyridine-CN.

Table 1.

UV-Visible Absorption Data

Compound	λ_{max} (nm)
ret-pyr-CN	446
car-pyr-CN	502
Re(I)-ret-pyr-CN	464 ^a , 511 ^b
Re(I)-car-pyr-CN	522 ^a , 612 ^b
Pt(II)-ret-pyr-CN	458 ^a , 481 ^b
Pt(II)-car-pyr-CN	542 ^a

^aAcetonitrile (solvent)

^bMethylene chloride (solvent)

Table 2.

Mass spectral Pt(II)-ret-analysis data^a

Compound	Molecular Ion Peak (m/z)
Re(I)-ret-pyr-CN	811 (ESI)
Re(I)-car-pyr-CN	943 (FAB)

^aMethanol (solvent)

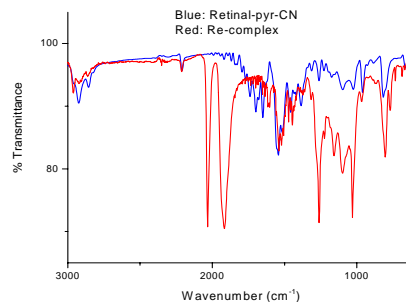


Fig. 2. Infrared spectra.

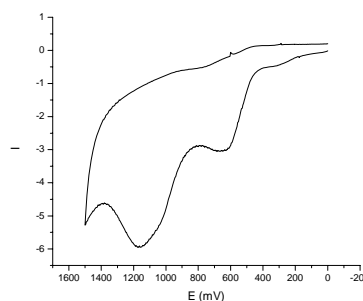


Fig. 3 CV of Re(I)-car-pyr-CN

3. Conclusion

Metal complexes of all-trans-retinal and β -apo-8'-carotenal derivatives have been synthesized and showed solvatochromism and irreversible oxidation potentials.

4. Acknowledgments

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