Heteroleptic Complexes Based on Heteroarylimidazolic Ligands

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Abstract
This project aims at the synthesis and characterization of different heteroleptic ruthenium(II) complexes based on heteroarylimidazolic ligands. For this purpose, two series were developed: the first, based on derivatives of dichlorobis(2,2'-bipyridine)ruthenium(II) complex; the second starts with the synthesis of the ligand 2,6-di(1H-imidazol-2-yl)pyridine and the formation of its complex with ruthenium.

Key words: ruthenium, heteroleptic complexes, imidazoles.

Introduction

N-heterocyclic aromatic ligands have been widely studied in coordination chemistry due to their rigid structures and electronic conjugated systems, which favors complexes with high absorptivity in the UV-Vis region. Based on this, the main interest is to develop complexes with other N-heterocycles and the use of derivatives of imidazole ligands to explore different electronic structures and reactivities due to the possibility of deprotonation or derivatization of imidazole.

Results and Discussion

The complex dichlorobis(2,2'bipyridine)ruthenium(II) was synthesized according to the method described by Sullivan et al.1 In the following step, the labile chlorides were replaced by ligands of the type 2-(1H-imidazol-2-yl)heteroaryl, previously produced by our research group. The heteroaryl was varied among pyridine, pyrimidine and pyrazine (Figure 1 (1)).

To the other series of complexes, the ligand 2,6-di(1H-imidazol-2-yl)pyridine was synthesized by the method proposed by Voss et al.2 According to the method described by Hashiguchi et al.3, the complex trichloro(2,6-di(1H-imidazol-2-yl)pyridine)ruthenium(III) was produced. Posteriorly, two of the chlorides were replaced by the ligands previously used – with heteroaryl as pyridine and pyrazine (Figure 1 (2)). Yields below 40% were achieved in both steps leading to the necessity of researches for an alternative route.

Figure 1. Structures of some of the products obtained, where heteroaryl used was pyridine in both cases.

The products were characterized by ESI-MS, ¹H NMR, spectroscopy in the UV-Vis and IR region. The results were compared with those reported in the literature where available. Next, the UV-Vis spectra of two of the complexes obtained from dichlorobis(2,2'bipyridine)ruthenium(II) (Figure 2), that illustrates the change in MLCT band caused only by modifying the heteroaryl group of 2-(1H-imidazol-2-yl)heteroaryl ligand.

Conclusions

Despite the initial difficulties to obtain dichlorobis(2,2'-bipyridine)ruthenium(II), the sequential addition of 2-(1H-imidazol-2-yl) heteroaryl ligands led to yields near to 78%. Furthermore, the ligand 2,6-di(1H-imidazol-2-yl)pyridine has been successfully synthesized, with average yield of 76%. However, obtaining the complex of this ligand with ruthenium has proved to be a challenge, and there is a need to improve the synthesis proposed in the literature, which is still under development.

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