

Abstract

This PhD thesis is a summary of my research, which I have achieved since 2011r in Department of Crystallography Institute of Chemistry University of Silesia under supervision of Prof. Jan Grzegorz Małecki. Research conducted by me in this area has focused on structural and spectroscopic characterization of phosphine ruthenium(II) complexes, obtained on the basis of the precursors $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ and $[\text{RuCl}_2(\text{PPh}_3)_3]$ with N-heteroaromatic ligands. As part of the work, I obtained 30 coordination compounds of ruthenium(II), which can be divided into three groups: pseudohalide derivatives of the starting compounds $[\text{RuH}(\text{X})(\text{CO})(\text{PPh}_3)_3]$ (where $\text{X} = \text{N}_3^-$, NCO^-); $[\text{RuH}(\text{X})(\text{CO})(\text{PPh}_3)_2(\text{MeCN})]$ and $[\text{Ru}(\text{X})_2(\text{PPh}_3)_2(\text{MeCN})_2]$ (where $\text{X} = \text{N}_3^-$, NCS^-); complexes with bidentate N,X-donor ($\text{X} = \text{N}$, O) ligands with general formula $[\text{RuH}(\text{CO})(\text{L})(\text{PPh}_3)_2]$ and $[\text{Ru}(\text{L})_2(\text{PPh}_3)_2]$ (where L – bidentate N,O- or N,N-donor ligands); chloride and pseudohalide ruthenium(II) with N-heteroaromatic monodentate N-donor ligands with general formula $[\text{RuHX}(\text{CO})(\text{L})(\text{PPh}_3)_2]$ (with $\text{X} = \text{Cl}$, NCO , N_3 , NCS , $\text{L} =$ monodentate N-heterocyclic ligand). The resulting compounds were characterized by structural and spectroscopic study with particular emphasis on electron emission spectra. The discussion of the experimental results was expanded to include the results of quantum-mechanical calculations. The crystal and molecular structure of coordination compounds was uniquely determined by X-ray structural analysis.

The study on emission spectra of the compounds $[\text{RuH}(\text{X})(\text{CO})(\text{PPh}_3)_2(\text{MeCN})]$ and $[\text{Ru}(\text{X})_2(\text{PPh}_3)_2(\text{MeCN})_2]$ (where $\text{X} = \text{N}_3^-$, NCS^-) at both ambient and low temperature showed the mixed nature of the emissive excited state (*LLCT/MLCT*) and the effect of thermal deactivation process of the excited states to the *MC*, which is characteristic also for the other two groups of received complexes. In contrast, lack of luminescence characteristic for $[\text{RuH}(\text{X})(\text{CO})(\text{PPh}_3)_3]$ (wherein $\text{X} = \text{N}_3^-$, NCO^-) can be related to the deviations from an ideal octahedral geometry due to steric hindrance caused by the presence of three triphenylphosphine ligands.

The second group of received complexes are compounds with bidentate N,O- and N,N-donor ligands. Among them large group are compounds with general formulas $[\text{RuH}(\text{CO})(\text{L})(\text{PPh}_3)_2]$ and $[\text{Ru}(\text{L})_2(\text{PPh}_3)_2]$ (where L – carboxylate derivative N-heteroaromatic). On the basis of the electronic structure of these compounds, excited states was identified as *MLCT* with an admixture of *ILCT*. Excitation in the ultraviolet range result in emission bands including the range from the near ultraviolet and blue color of visible light. In contrast, excitation and emission spectra of $[\text{RuH}(\text{CO})(\text{L})(\text{PPh}_3)_2]$ (wherein L - derivatives of 8-hydroxyquinoline) relative to the emission spectra in the previous group are bathochromic shifted, which extends the spectral range of emission in the study compounds to green and red-orange color. Moreover, in this group of compounds the fluorescence resonance energy transfer (FRET) between the states *IL* and *MLCT* have place.

Chloride and pseudohalide complexes with monodentate N-heteroaromatic ligands was also obtained and characterized. In a series of compounds with 4-pyrrolidinopyridine, impact of π^* triphenylphosphine on the electronic transitions corresponding to the excited wavelengths was detected, and for compounds with 4-(4-nitrobenzyl)pyridine share of π^* pyridine ligand was visible. The influence of pseudohalide ligands to the HOMO was illustrated by density of state diagrams, and on this basis it has been found that character of emissive excited state in chloride complexes can be defined as *MLCT*, however in the case of pseudohalide derivatives excited state are *MLLCT* or *LLCT*.

Quantum yields in the obtained compounds are in the range from a few to several percent, with higher emission quantum yields determined for compounds with bidentate ligands than for chloride and pseudohalide coordination compounds with monodentate ligands. Nanosecond lifetimes of excited states (at room temperature) show significant share of thermal deactivation of *MLCT* excited states.

One of the aspects which are characteristic for most of known from the literature coordination compounds of ruthenium (II) is that the luminescence of such systems is usually limited to the range of red and orange. One of the undertaken research problem was to check whether it is possible to obtain emission maxima in a wider spectral range. Phosphine ruthenium (II) complexes with N-heteroaromatic ligands show emissions in higher field of energy, thus extending the spectral range of emission of coordination compounds of this element.