Joint meeting

VII Latin American Crystallographic Association

and

XXVII Brazilian Crystallographic Association

BOOK OF ABSTRACTS

October 14 to 17, 2025

Fortaleza, Brazil

STRUCTURAL AND BIOLOGICAL ASPECTS OF RU(II) COMPLEXES WITH β-DIKETONES

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Seven new Ruthenium complexes Ru1–Ru7 were synthesized using different β-diketones ligands. Five of those were fluorinated asymmetric β-diketones, and the other two are symmetric ones. The complexes were characterized by Cyclic Voltammetry (CV), UV/vis spectroscopy (UV-Vis), Infrared spectroscopy (IR), Mass Spectrometry (MS), ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR, and single-crystal X-ray diffraction (SCXRD). CV shows that all complexes were more stable than the precursor, with anodic peak potential of 700 mV. UV-Vis shows major electronic transitions of π–π due to the aromatic rings of triphenylphosphine (PPh_3) and phenanthroline (Phen). In IR, the stretch of the carbonyl bond was observed to be shifted to a lower energy region due to electron density sharing with the metal. Other vibrational modes were observed, related to PF_6, C–P bonds, and C–H bonds. MS shows the molecular ion mass as expected, but also a fragmentation of the complex with a PPh_3 release. This also motivated the search for complex stability in other solvents such as DMSO, DMF, and acetonitrile. Specifically for DMSO, it was observed that after 6 hours, the complex showed no further change in the UV-Vis spectrum, and it was also confirmed that the complex remained stable after 6 hours in ^{31}P-NMR. The complex and precursor show both a very similar ^{31}P-NMR spectrum, with both showing a singlet signal at 25 ppm, but also for the final complex a septet due to PF_6 counter-ion coupling. ^{1}H-NMR confirmed the expected structure, and it was observed that the complexes with more aromatic rings Ru1, (Ru1 > Ru2 > Ru3), show PPh_3 hydrogens in a narrower range than Ru3, which shows PPh_3 hydrogens in a wider range. This observation was related to the π–π interaction observed for those complexes in SCXRD. The complexes also show an octahedral-like geometry, confirming the expected structure, with triclinic and monoclinic crystal system, with only one complex being non-centrosymmetric. The two PPh_3 groups show different conformations in the complexes: eclipsed and staggered conformations. This was observed due to the rotational freedom of the Ru-P bond. The β-diketone ligands also show a decrease in C-O bond length due to deprotonation and coordination to the metal. Hirshfeld surface and fingerprint analyses show that the major interactions observed were due to H…H interactions in all complexes. Complexes with CF_3 groups also show high percentage H…F interactions, in some cases even greater than H…C interactions. The complexes were also studied for their cytotoxic activity against lung and breast cancer cell lines. All complexes show better results than cisplatin in lung cancer lines. Complexes Ru4 and Ru5 have IC_{50} values around 0.64 uM, which are 15 times more active than cisplatin (11.54 uM). DNA interaction studies were performed by viscosity analysis, DNA titration, and circular dichroism, but no strong interactions were observed.

Keywords: Bioinorganic; SCXRD; Ruthenium; β-diketones; Cancer; Cytotoxic.

F. Niquini thanks FAPEMIG for the master's scholarship 5.43/2021, and CNPq for the current doctoral scholarship 141475/2023-4. All authors would like to thank FAPEMIG, CNPq, FAPESP, and CAPES for direct or indirect support, and the universities involved for all support during the development of this work.