

Nitrosyl ruthenium complexes with diflunisal and 2,4-dihydroxybenzoate ligands: synthesis, characterization and reactivity

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The key role of nitric oxide (NO) in a wide range of biological processes has increased the interest on metal nitrosyls as NO donors.¹ One strategy to improve biological activity of these complexes is the use of bioactive co-ligands. With this aim we report the synthesis, characterization as well as chemical and electrochemical reactivity of the Na₂[Ru(NO)Cl₃(DF)] (**I**) and the Na[Ru(NO)(OH)₂(2,4DHB)(OH₂)] (**II**) complexes. These complexes contain Diflunisal (DF) which is a nonsteroidal anti-inflammatory agent and 2,4-dihydroxybenzoic acid (2,4DHB) which has antioxidant activity as co-ligands. Both complexes were synthesized from Ru(NO)Cl₃.H₂O. Characterization of complexes **I** and **II** by ¹H-NMR and CNH microanalysis support the proposed formulations. The FTIR spectra of **I** and **II** showed intense bands at 1880 and 1873 cm⁻¹ which were assigned to ν(NO)¹, and ν(C=O) at 1614 and 1633 cm⁻¹, respectively. These bands are shifted in comparison with the free ligands (1690 cm⁻¹ for DF and 1649 cm⁻¹ for 2,4DHB). The difference between the wavenumber of the symmetric bending vibrations and asymmetric bending of carboxylate (COO) group is lower than 200 cm⁻¹ which suggest that DF and 2,4DHB are coordinated by one oxygen atom of COO group.² The electronic spectra of **I** and **II** showed IL bands (π - π*) at 326 nm (ε = 3.0×10³ M⁻¹.cm⁻¹) and 210 and 250 nm (ε = 3.9×10⁴ and 1.5×10⁴ M⁻¹.cm⁻¹), respectively. Complex **I** also showed one band at 381 nm (ε = 1.7×10³ M⁻¹.cm⁻¹) tentatively assigned to MLCT (dπ - π*) transition and complex **II** also showed one band at 295 nm (ε = 8,4 x 10³ M⁻¹.cm⁻¹) tentatively assigned to IL with d-d transition contribution. DPV (vs Ag/AgCl) for **I** (ACN/HCl/KCl 0.1 M) showed {RuNO}^{6/7} process at -420 mV (E_{cp1}) and one anodic peak at +1122 mV assigned to DF redox centered process. Complex **II** (ACN/acetate buffer 0.1 M pH 4.4) showed {RuNO}^{6/7} process at -598 mV (E_{cp2}) and 2,4DHB redox centered processes at +980 mV (E_{ap1}), +1185 mV (E_{ap2}) and -1000 mV (E_{cp1}). Electrolysis at -750 mV (vs Ag/AgCl) or chemical reduction with zinc amalgam showed current intensity decrease of {RuNO}^{6/7} process for both complexes. FTIR of reduced complexes showed a decrease (for **I**) or disappearance (for **II**) of the ν(NO) band. These data indicate **I** and **II** can be potential NO donors after reduction. Furthermore, they can have anti-inflammatory or antioxidant activities from co-ligands which could be improved by NO release.

¹Tfouni, E.; Krieger, M.; McGarvey, B. R.; Franco, D. W.; *Coord. Chem. Rev.* 2003, 236, 57.

²Siddiqi, Z. A.; Ansari, I. A.; Sama, F.; Shahid, M.; *Int. J. Inn. Res. Sci. Eng. Tec.* 2014, 3, 8673.