Synthesis and characterization of *cis*-[Ru(tmp)2(CH3CN)2](NO3)2·EtOH; FS-DNA interaction and electrocatalytic reduction of CO2 to CO

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Abstract

The mononuclear Ru(II) complex, *cis*-[Ru(tmp)$_2$(CH$_3$CN)$_2$](NO$_3$)$_2$·EtOH, where tmp is 3,4,7,8-tetramethyl-1, 10-phenanthroline, has been prepared and characterized by elemental analysis, spectroscopic methods (UV-Vis and FT-IR) and single crystal X-ray structure analysis. This complex crystallized in the monoclinic crystal system with a space group of *P*2(1)/c and the following unit cell parameters: *a* (Å) = 11.1599(3), *b* (Å) = 17.5396(4), *c* (Å) = 19.0239(4), *α* (˚)= 90, *β* (˚)= 91.3210, *γ* (˚)= 90, *Z* = 2 and *V* (Å^3) = 3722.75(15). The X-ray analysis of the complex shows that the coordination geometry around the Ru(II) center is a distorted octahedral. Through two acetonitrile molecules in the *cis* positions and two bidentate tmp ligands. The interaction of the complex with fish sperm DNA (FS-DNA) has been monitored by UV-Vis, fluorescence titration and voltammetric (CV and DPV) techniques. In UV-Vis experiments, a significant hypochromic shift in the $\pi \rightarrow \pi^*$ transition with red shift was observed upon addition of FS-DNA and the intrinsic binding constant (K_b = 1 × 10^3 M^{-1}) was determined. The emission intensity of the complex in the presence of FS-DNA gradually quenched which implies the photoelectron transfer from the guanine base of DNA to the MLCT state of the complex. The results reveal that the complex binds to FS-DNA by a groove binding mode. Also, the electrocatalytic reduction of CO2 to CO by *cis*-[Ru(tmp)2(CH3CN)2](NO3)2·EtOH has investigated with cyclic voltammetry technique. The CV data showed that the multi-electron reduction of CO2 was catalyzed by the metal complex and a mechanism was proposed for this multi-step reduction.

Keywords
X-ray crystallography; Ruthenium; 3,4,7,8- tetramethyl-1,10-phenanthroline; Polypyridyl complexes; DNA-binding; Groove mode; Electrocatalytic reduction