Title

Quantum-mechanical study of a MO2(cyclam)+ complexes series with M = Mn, Tc, Re

Abstract

This work focuses on the theoretical study of nd2 pentavalent group 7 metal ions (Mn, Tc, Re) electronic structures complexed with cyclam (MO2(cyclam)+) via DFT due to their fascinating photochemical and electrochemical properties. Optical properties were studied via TD-DFT modeling ground (S0) and first excited (S1 and T1) states including spin–orbit effect induced in the absorption and emission spectra. Metal-ligand interactions were studied via EDA-NOCV analysis. DFT suggests increase stability as the metal gets bigger. MLCT and LMCT mechanisms can modulate the optical properties of cyclam ligand and could confer photocatalytic properties under visible light. Deactivation mechanisms shows dark states in all studied complexes. EDA-NOCV results show metal/cyclam interaction with covalent character for all systems, while the metal/oxygens interaction presents large electrostatic character where charge flow happens from cyclam ligand toward nd2-metal orbitals. All theoretical results suggest that MnO2(cyclam)+(a) will display similar properties to reported compounds TcO2(cyclam)+(b) and (ReO2(cyclam)+(c). © 2023 Elsevier B.V.

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