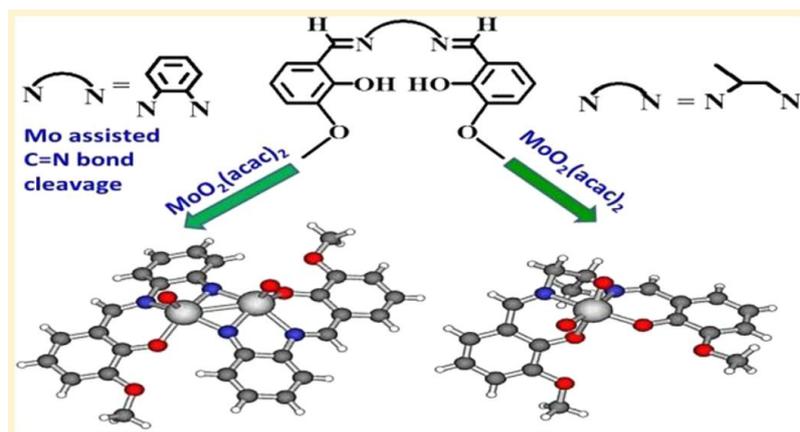


Monomeric and Dimeric Oxidomolybdenum(V and VI) Complexes, Cytotoxicity, and DNA Interaction Studies: Molybdenum Assisted C=N Bond Cleavage of Salophen Ligands

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Four novel dimeric bis- μ -imido bridged metal–metal bonded oxidomolybdenum(V) complexes $[\text{Mo}^{\text{V}}_2\text{O}_2\text{L}'_2]^{1-4}$ (1–4) (where L'^{1-4} are rearranged ligands formed in situ from H_2L^{1-4}) and a new mononuclear dioxidomolybdenum(VI) complex $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^5]$ (5) synthesized from salen type N_2O_2 ligands are reported. This rare series of imido-bridged complexes (1–4) have been furnished from rearranged $\text{H}_3\text{L}'^{1-4}$ ligands, containing an aromatic diimine (o-phenylenediamine) “linker”, where Mo assisted hydrolysis followed by –C=N bond cleavage of one of the arms of the ligand H_2L^{1-4} took place. A monomeric molybdenum(V) intermediate species $[\text{Mo}^{\text{V}}\text{O}(\text{HL}'^{1-4})(\text{OEt})]$ (Id^{1-4}) was generated in situ. The concomitant deprotonation and dimerization of two molybdenum(V) intermediate species (Id^{1-4}) ultimately resulted in the formation of a bis- μ -imido bridge between the two molybdenum centers of $[\text{Mo}^{\text{V}}_2\text{O}_2\text{L}'_2]^{1-4}$ (1–4). The mechanism of formation of 1–4 has been discussed, and one of the rare intermediate monomeric molybdenum(V) species Id^4 has been isolated in the solid state and characterized. The monomeric dioxidomolybdenum(VI) complex $[\text{Mo}^{\text{VI}}\text{O}_2\text{L}^5]$ (5) was prepared from the ligand H_2L^5 where the aromatic “linker” was replaced by an aliphatic diimine (1,2-diaminopropane). All the ligands and complexes have been characterized by elemental analysis, IR, UV–vis spectroscopy, NMR, ESI-MS, and cyclic voltammetry, and the structural features of 1, 2, 4, and 5 have been solved by X-ray crystallography. The DNA binding and cleavage activity of 1–5 have been explored. The complexes interact with CT-DNA by the groove binding mode, and the binding constants range between 10^3 and 10^4 M^{-1} . Fairly good photoinduced cleavage of pUC19 supercoiled plasmid DNA was exhibited by all the complexes, with 4 showing the most promising photoinduced DNA cleavage activity of $\sim 93\%$. Moreover, in vitro cytotoxic activity of all the complexes was evaluated by MTT assay, which reveals that the complexes induce cell death in MCF-7 (human breast adenocarcinoma) and HCT-15 (colon cancer) cell lines. (More in *Inorganic Chemistry* 2017, 56, 11190. DOI: 10.1021/acs.inorgchem.7b01578)