The Metal-NO Interaction in the Simple Redox System $[Cl_5Os(NO)]^{n-}$, n = 1-3: Structural and Spectroscopic Effects

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Experimental and computational results for the two-step redox system $[Cl_5Os(NO)]^{n-}$ (n = 1-3) are reported and discussed in comparison to the related one-step systems $[Cl_5Ru(NO)]^{n-}$ (n = 1,2) and $[Cl_5Ir(NO)]^{n-}$ (n = 1,2). In that series the osmium complex exhibits the lowest oxidation and reduction potentials. DFT Calculations of the structures reveal an increasing labilization of the bond to the *trans*-positioned chloride in the order M = Ir < Os < Ru. Accordingly, the reduced form $[Cl_5Os(NO)]^{3-}$ could be obtained only at –70°C in n-butyronitrile solution. EPR and IR spectroelectrochemical results are supported by DFT calculations: The oxidation of $[Cl_5Os(NO)]^{2-}$ occurs largely on the metal (spin density 0.711/0.892), the HOMO of the precursor being composed of Os 5d (63%) and Cl_{eq} 3p orbitals (36%). The reduction is more NO centered (spin density 0.454/0.563), the LUMO of $[Cl_5Os(NO)]^{2-}$ contains 65% π^*(NO) character with significant 5d Os contributions (33%). A rather large degree of metal-NO back donation in the $\{OsNO\}^7$ configuration of $[Cl_5Os(NO)]^{3-}$ which leads to an unusual low value of 1513 cm^{-1} for ν(NO), signifying contributions from an $Os^{III}(NO^-)$ formulation. Detailed analyses of the *g* anisotropy suggest that the different reduced species reported for $[Cl_5Os(NO)]^{3-}$ in AgCl host lattices may differ by eclipsed or staggered conformation of the bent NO^- axial ligand relative to the $Os^{II}Cl_4$ equatorial plane. The staggered form is calculated to be more stable by 0.013 eV = 105 cm^{-1}.