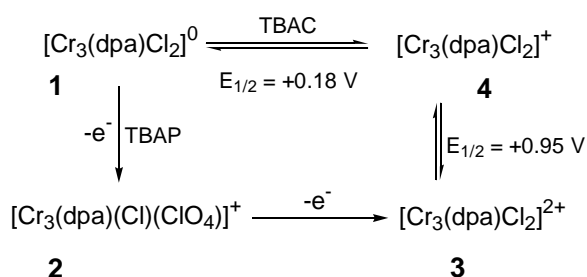


The Electrochemistry and Spectroelectrochemistry of
Linear Multinuclear Metal String Complexes

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The electrochemical properties of linear multinuclear metal string complexes have been studied by cyclic voltammetry (CV) and spectroelectrochemistry. $[\text{Cr}_3(\text{dpa})_4\text{Cl}_2]$, where dpa is the anion of bis(2-pyridyl)amine, exhibits two reversible redox couples at $E_{1/2} = +0.18$ and $+0.95$ V in CH_2Cl_2 . The one electron oxidation species might be $[\text{Cr}_3(\text{dpa})_4(\text{Cl})(\text{ClO}_4)](\text{ClO}_4)$. The two-electron oxidized product is unstable and proceeds auto-reduction reaction to form $[\text{Cr}_3(\text{dpa})_4\text{Cl}_2](\text{ClO}_4)$, which has been structurally characterized.



Similar to the trichromium complex $[\text{Cr}_3(\text{dpa})_4\text{Cl}_2]$, both penta- and heptachromium complexes show two redox couples at 0.29 and 0.63 V, and 0.25 and 0.45 V, respectively. These one and two-electron oxidation products are stable and have been structurally characterized.

$[\text{Co}_3(\text{dpa})_4\text{Cl}_2]$ shows two reversible redox couples at $E_{1/2} = +0.43$ and $+1.34$ V in CH_2Cl_2 . One-electron oxidation generates a stable product and this product is characterized as $[\text{Co}_3(\text{dpa})_4\text{Cl}_2](\text{ClO}_4)$. The X-ray crystal structures of $[\text{Cr}_3(\text{dpa})_4\text{Cl}_2](\text{ClO}_4)$ and $[\text{Co}_3(\text{dpa})_4\text{Cl}_2](\text{ClO}_4)$ generated by electrochemistry are comparable with those by chemical methods.

In the pentanuclear cobalt complexes, two reversible redox couples at about $+0.35$ and $+0.85$ V, respectively, are observed. The first oxidation is a metal-centered reaction and the product is structurally characterized. The Co-Co and Co-N bond distances are not significantly different from those of the neutral analogues whereas the Co-X (X = axial ligand) bond lengths exhibit a slight decrease. The second oxidation product is stable at the time scale of spectroelectrochemistry, but proceeds auto-reduction and forms the corresponding one-electron oxidation product under the crystallization conditions.

In the multinuclear nickel complexes, our preliminary electrochemical results show that the potentials of the first one-electron oxidation for tri-, penta-, and heptanickel complexes are 1.02, 0.65, and 0.18 V (vs. Ag/AgCl), respectively. The descending trend on the first oxidation potential indicates that there are interactions among the nickel atoms in this series of multinuclear complexes.