

# **Structures and Reactions of Diplatinum Complexes**

Thesis by  
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Now, on to the next adventure!

## ABSTRACT

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A  $d^8-d^8$  complex  $[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{BF}_2)_4]^{4-}$  (abbreviated  $\text{Pt}(\text{pop-BF}_2)^{4-}$ ) undergoes two  $1e^-$  reductions at  $E_{1/2} = -1.68$  and  $E_p = -2.46$  V (vs  $\text{Fc}^+/\text{Fc}$ ) producing reduced  $\text{Pt}(\text{pop-BF}_2)^{5-}$  and superreduced  $\text{Pt}(\text{pop-BF}_2)^{6-}$  species, respectively. The EPR spectrum of  $\text{Pt}(\text{pop-BF}_2)^{5-}$  and UV-vis spectra of both the reduced and the superreduced complexes, together with TD-DFT calculations, reveal successive filling of the  $6p\sigma$  orbital accompanied by gradual strengthening of Pt–Pt bonding interactions and, because of  $6p\sigma$  delocalization, of Pt–P bonds in the course of the two reductions. Both reduction steps proceed without changing either  $d^8$  Pt electronic configuration, making the superreduced  $\text{Pt}(\text{pop-BF}_2)^{6-}$  a very rare  $6p^2$   $\sigma$ -bonded binuclear complex. However, the Pt–Pt  $\sigma$  bonding interaction is limited by the relatively long bridging-ligand-imposed Pt–Pt distance accompanied by repulsive electronic congestion.  $\text{Pt}(\text{pop-BF}_2)^{4-}$  is predicted to be a very strong photooxidant (potentials of +1.57 and +0.86 V are estimated for the singlet and triplet  $d\sigma^*p\sigma$  excited states, respectively).

Further study of the electronic excited states of  $\text{Pt}(\text{pop-BF}_2)^{4-}$  in the presence of luminescence quenchers revealed Stern-Volmer type dynamic quenching of the triplet state by trialkyl and triaryl amines. Quenching of the singlet as well as the triplet was observed in the presence of  $\text{Co}^{II}$  trisbipyridine complexes, but sample decomposition and the observed presence of simultaneous static and dynamic quenching behaviors hampered quantitative analysis.

## PUBLISHED CONTENT AND CONTRIBUTIONS

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T.V.D. participated in the conception of the project; conducted absorption, electron paramagnetic resonance, electrochemical, and spectroelectrochemical experiments; prepared and analyzed data; and participated in the writing of the manuscript.

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