

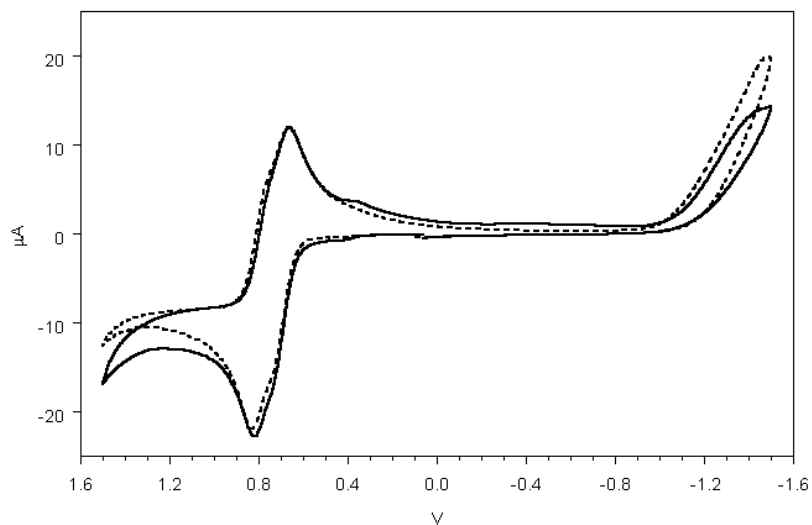
Experimental Supplemental Information

"Cyclometallated Pt^{II} and Pd^{II} Complexes with a Trithiacrown Ligand"

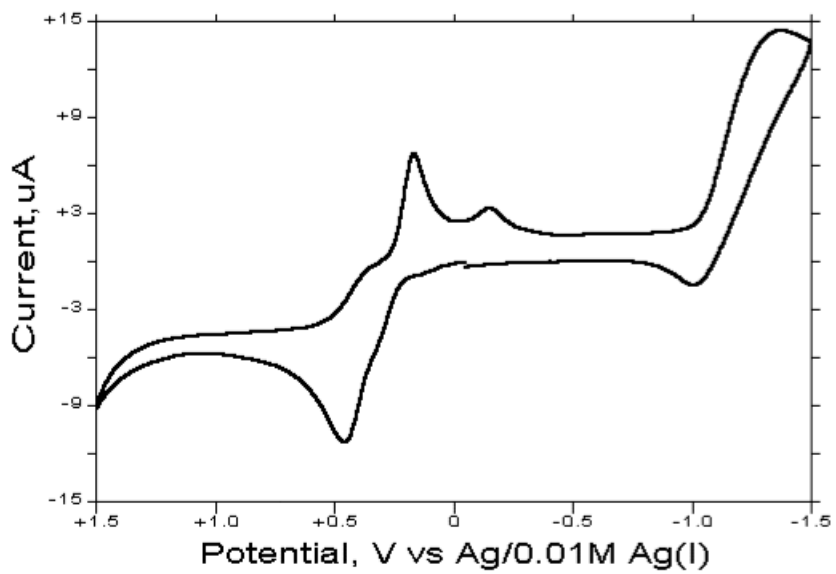
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1. Electrochemical Data

A. Cyclic voltammograms of [Pd([9]aneS₃)(ppy)](PF₆) (**1**) (solid line) and [Pd([9]aneS₃)(bzq)](PF₆) (**2**) (dotted line). Measured in MeCN at 2 mM in 0.1 M TBABF₄ using a Pt disk working electrode.



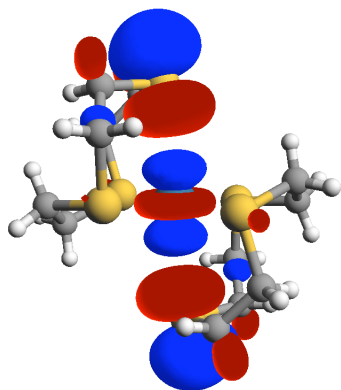
B. Cyclic voltammogram of $[\text{Pt}([\text{9}]\text{aneS}_3)(\text{bzq})](\text{PF}_6)$. Measured in MeCN at 2 mM in 0.1 M TBABF₄ using a Pt disk working electrode.



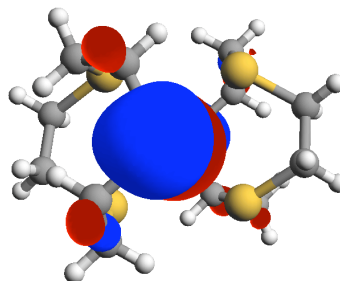
2. DFT Calculations

a. $[\text{Pt}(\text{[9]aneS}_3)_2]^{2+}$

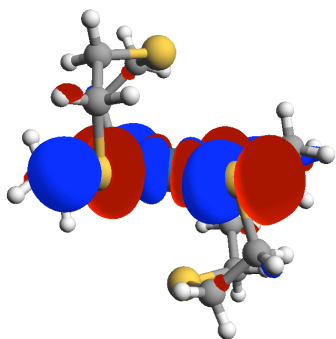
HOMO



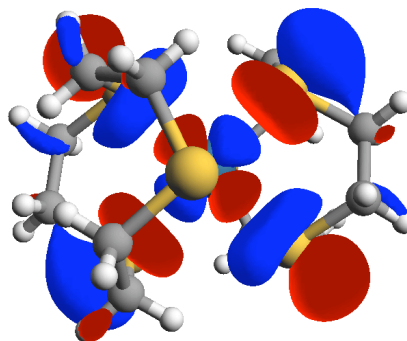
HOMO at 90°



LUMO

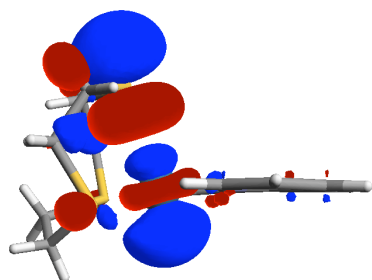


LUMO at 90°

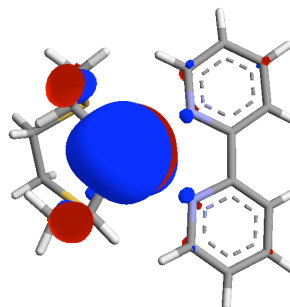


b. [Pt([9]aneS₃)(bipy)]²⁺

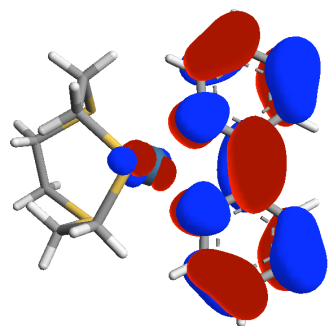
HOMO



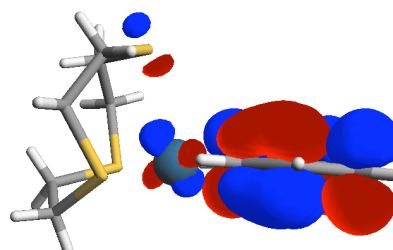
HOMO at 90°



LUMO

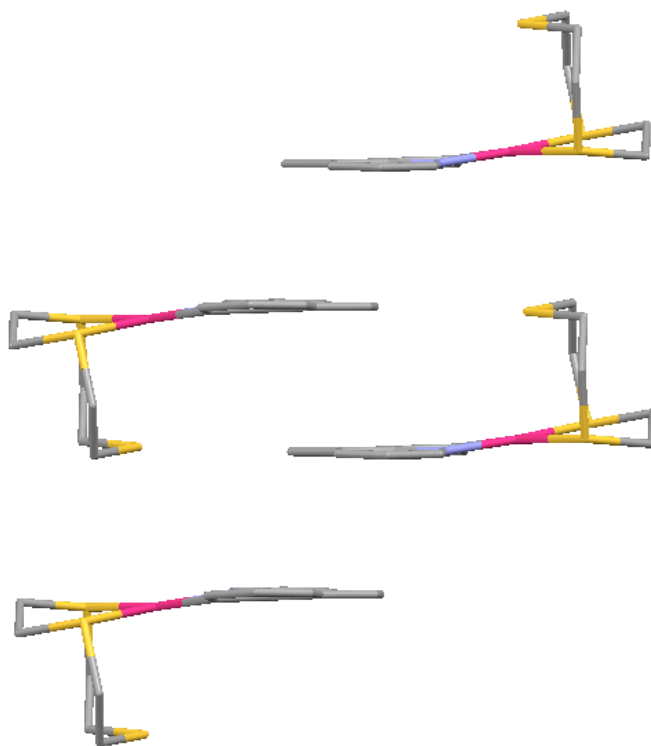


LUMO at 90°

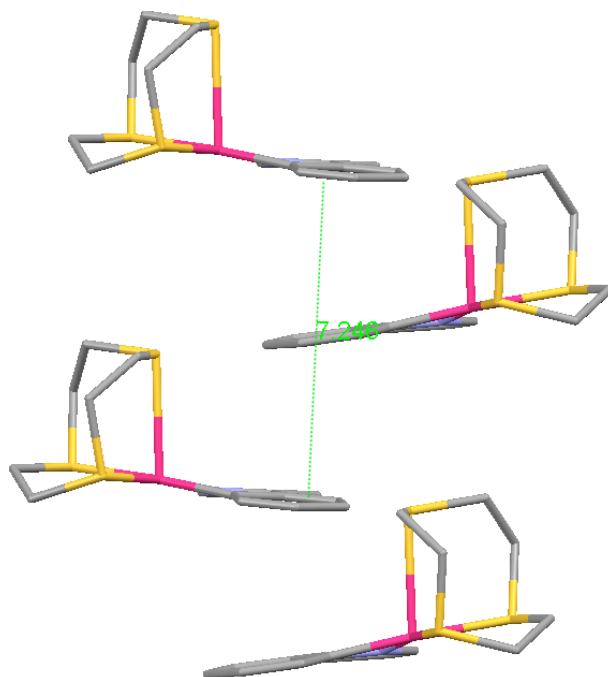


C. Intermolecular Packing Motifs, π - π Stacking Shown by Pt(II) and Pd(II) [9]aneS₃ Complexes with Diimine and Cyclometallating Ligands.

Stacking Motif A. Alternating *in-in* and *out-out* layers. Stacking is shown for Complex **2**, [Pd([9]aneS₃)(bzq)](PF₆). The π -stacking distances between bzq ligands are 3.20 Å for the shorter *out-out* orientation and 3.41 Å for the longer *in-in* orientation.



Stacking Motif B. Non-parallel layers. Stacking for Compound **1**, $[\text{Pd}([\text{9}]\text{aneS}_3)(\text{ppy})](\text{PF}_6)$, is shown. Angles between adjacent ppy planes are 9.5°



Stacking Motif C. Isolated dimers; may be either *out-out* or *in-in*

Out-out dimer for Complex **3**, [Pt([9]aneS₃)(bzq)](PF₆), is shown.

