The Coordination Chemistry of Redox Noninnocent *o*-Aminophenol and Dithiolene Ligands with Transition Metal Ions

o-Aminophenols constitute an archetypal class of redox-active, noninnocent ligands. The term 'noninnocent' is widely used to emphasize the idea that these ligands do not necessarily possess a closed-shell configuration. Therefore, they can coordinate to a central metal ion in distinctly different oxidation and protonation levels, as single or doubly deprotonated forms and can be oxidized to the monoanionic radical form and finally to a neutral quinone form. These oxidation states of the ligands in the coordination compounds are characterized by their differing C-O, C-N, and C-C bond distances. Low temperature X-ray crystal studies are capable of providing identification for these different oxidation levels of the respective ligands in a given transition metal complex.

Similarly, *cis*-1,2–disubstituted ethylene–1,2 dithiolato ligands also belong to the class of noninnocent ligands. An increase in the ethylene C=C bond and a decrease in the C-S bonds were adopted upon oxidation of a dianionic thiolate to a monoanionic radical.

Discrepancies arise in many complexes with noninnocent ligands regarding metal and ligand oxidation states. To clarify these ambiguities arised we have decided to resynthesize and characterize some analogues complexes to have proper understanding of the electronic structures of the complexes.

A series of square planar complexes of Co, Ni, and Pd containing bulky *N,O*-coordinated noninnocent 2-(2-trifluoromethyl)anilino-4,6-di-*tert*-butylphenol ligand and Au complexes containing *S,S*-coordinated dithiolene ligands were synthesized.

The low temperature crystal structures of square planar cobalt complexes clarify all the discrepancies that have arisen. Therefore assignment of the spectroscopic oxidation state of the central cobalt ion as +III has been achieved. Structural information together with the spectroscopic data allowed to understand the proper electronic structure of the square planar Ni, Pd, and Au complexes with noninnocent *o*-aminophenol and dithiolene ligands in different oxidation states.