

SUMMARY

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I

The known chemistry of azo compounds with special reference to their metallo-derivatives has been briefly reviewed in Chapter I. A brief discussion on relevance of platinum metal complexes with azo ligands has also made. The purpose of the present investigation is cast on this background.

II

The reaction of a group of terdentate ligands having O,N,S donor set, 2-hydroxy-1-(2'-alkylthiophenylazo)naphthalenes and 1-hydroxy-2-(2'-alkylthiophenylazo)naphthalenes, with sodium tetrachloropalladate at room temperature leads to the formation of complexes of the type $[Pd(L)Cl]$. All the palladium compounds have been isolated in pure form and characterized by spectral and elemental analysis data. The crystal structures of $[Pd(L)Cl]$ have been determined by single crystal X-ray diffraction as representative cases. The crystal structures show that the complexes are of distorted square-planer structures in which palladium(II) centers are bonded to O1 of the naphtholato function, N2 of the diazene group and S1 at the 2' position of the phenyl fragment. The fourth coordination position is occupied by a chloride ion. These complexes show the intense absorption in the visible region and the nature of the electronic transitions has been examined using TD-DFT formalism.

III

Di- μ -chloro-bis(η^3 -2-methylallyl)platinum(II) smoothly reacts with 2-hydroxy-1-(2'-alkylthiophenylazo)naphthalenes and 1-hydroxy-2-(2'-alkylthiophenylazo)naphthalenes (HL) in chloroform and afford complexes of the type $[Pt^{II}LCl]$. All the

platinum complexes [Pt^{II}LCl] have been successfully characterized by spectroscopic techniques. The solid state structures of [Pt^{II}LCl] have been determined by single crystal X-ray diffraction. All the platinum(II) complexes absorb strongly in the ultraviolet and visible region. The TDDFT (time-dependent density functional theory) calculation has been carried out for better understanding of the electronic structure of divalent platinum complexes and the nature of spectral transitions. The TDDFT calculations reveal that the high energy and low energy absorptions are predominantly due to intraligand π - π^* and metal to ligand charge-transfer transitions respectively. The simulated spectra of the complexes are in agreement with the experimental electronic spectra. Compounds [Pt^{II}LCl] undergo facile oxidation reaction with halogens X₂ and the oxidized platinum complexes undergo rapid reductive elimination to afford the complexes [Pt^{II}L(X)] and ClX. The crystal structure of [Pt^{II}LX] has been determined by X-ray crystallography.

IV

Rhodium(I) selectively cleaves C(sp²)-S bond of 2-hydroxy-1-(2'-alkylthiophenylazo) naphthalenes and 1-hydroxy-2-(2'-alkylthiophenylazo) naphthalenes with concomitant two-electron metal based oxidation resulting in the formation of novel rhodium(III) cyclometallate. The molecular structures of the resulting complexes have been determined by single crystal X-ray crystallography. Rhodium(III) binds desulfurized modified HL ligands *via* O, N, C(aryl) donor set. Iridium(I) also selectively cleaves the C(sp²)-S bond of ligands (HL) with simultaneous two-electron metal based oxidation. The resulting iridium(III) cyclometallates have also been isolated and structurally characterized.

Cobalt(II), the remaining member of the group 9, cleaves the C(sp³)-S bond of the diazene ligands (HL¹-HL¹⁰) with concomitant one-electron oxidation leading to the formation of novel cobalt(III) complexes. The molecular structures of the resulting cobalt(III) complex has been determined by single crystal X-ray crystallography. The cobalt(III) center is bound to one monoanionic HL *via* O, N, S donor set along with a dianionic modified HL through O, N, S(thiol) donor set. Non-covalent interactions like C-H...Cl and π ... π interactions between adjacent aromatic rings have been observed in solid state. The electronic structures of the representative complexes have been examined using time-dependent density functional theory (TD-DFT).

V

Reaction of 2-hydroxy-1-(2'-alkylthiophenylazo)naphthalenes and 1-hydroxy-2-(2'-alkylthiophenylazo)naphthalenes (HL) with [Ru^{II}(PPh₃)₂Cl₂] in ethanol medium leads to formation of complexes of the type [Ru^{II}(L)(PPh₃)₂Cl]. In contrast, the diazene ligands (HL) react with RuCl₃ · xH₂O and form ruthenium(II) complexes of the type [Ru^{II}(L)₂]. All the ruthenium compounds have been isolated in pure form and characterized by spectroscopic (IR, electronic and NMR) data. The molecular structure of one representative member of [Ru^{II}(L)₂] has been determined by single crystal X-ray diffraction. All the complexes are diamagnetic (low spin d⁶, S=0). These complexes show intense MLCT transitions in the visible region and characteristic spectral properties.