

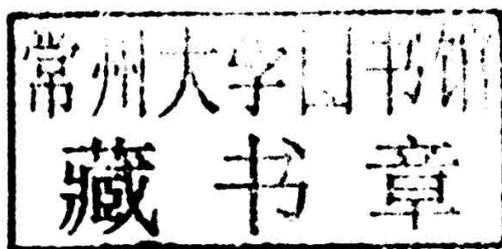
Sanjay Kumar Singh
Daya Shankar Pandey

Arene-ruthenium complexes containing nitrogen and oxygen donor ligands

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1.

Introduction

The chemistry of coordination compounds and organometallics is an important and challenging area of modern inorganic chemistry. Foundation of organometallic chemistry, the chemistry dealing with the study of compounds containing direct metal-carbon bonds, was first led by one of the unexpected discoveries of $\text{PtCl}_2(\text{C}_2\text{H}_4)\cdot\text{KCl}\cdot\text{H}_2\text{O}$ by W.C. Ziese in 1827, where platinum atom and the double bond of ethylene is π -bonded.¹ Further, the discovery of ferrocene in 1953 has added new dimensions to the organometallic chemistry.² Organometallic complexes with M-C π -bonds have found considerable attention due to the quite intriguing chemical properties of these π -complexes. Many π -complexes (sandwiched (or) half-sandwiched) having η^6 -arene (benzene and its substituted derivatives) and /or η^5 -cyclopentadienyl based ligands (pentamethylcyclopentadienyl, indenyl) are well known and extensively studied.³ In particular the *platinum group* metal complexes have received continuous attention of a large group of scientific community.^{3,4}

Ruthenium and rhodium complexes are particularly attractive targets for study as they have kinetically stable oxidation states, often reversible nature of redox couples, and relative ease with which mixed ligand complexes can be prepared. Ruthenium and rhodium metals offers a wide range of chemically and electrochemically accessible oxidation states {from oxidation state -2 in $[\text{Ru}(\text{CO})_4]^{2-}$ to $+8$ in RuO_4 for ruthenium, and -1 in $[\text{Rh}(\text{CO})_4]^-$ to $+5$ in $[\text{RhF}_6]^-$ for rhodium} therefore, their complexes are redox-active. Ruthenium and rhodium complexes exhibit a great deal of applications in many areas of chemistry.⁵

Most widely studied section of η^6 -arene d^6 -transition metal chemistry includes benzene and *p*-cymene as these are conveniently prepared, however related η^6 -arene ruthenium(II) complexes with hexamethylbenzene and 1,3,5-trimethylbenzene (mesitylene) are also in use. The bis(η^6 -arene) complexes can be easily prepared by reduction of transition metal halides in the presence of aromatic hydrocarbons or by facile arene exchange at higher temperature from the transition metal complexes as for $\eta^6\text{-C}_6\text{Me}_6$.^{6,7} The related η^5 -cyclopentadienyl based (C_5H_5 , C_5Me_5) transition metal complexes has been prepared by either direct reaction of pentamethylcyclopentadiene with metal halides or by sodium salt of cyclopentadiene

($\text{Na}^+\text{C}_5\text{H}_5^-$) with metal halides in THF.⁸ Since 1968, after the discovery of pentamethylcyclopentadienyl rhodium complex [$\{(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(\mu\text{-Cl})\text{Cl}\}_2$] by *J. Kang* and *P.M. Maitlis* this complex have become a valuable material for various reactions because of its unique combinations of inert C_5Me_5 ring with metal bonds, which survives in acidic and basic as well as reducing and oxidizing conditions and labile chloro ligands. It undergoes various reactions without loss of the ring including nucleophilic substitution, C-H activation, hydrogen transfer, oxidation and reduction, catalysis, as well as photochemical and bioinorganic transformations.⁹ Good solubility coupled with low sensitivity to air and moisture makes them easy to crystallize and stabilize unusual ligand systems. The chloro bridges are labile enough for the preparation of a large number of sequential air-stable complexes under mild reaction conditions.

Ruthenium η^6 -arene and η^5 -cp complexes and analogous rhodium complexes with *N,N'*-donor poly-pyridyl and pyridyl-azine ligands and *N,O*-donor Schiff base ligands have received considerable attention owing to their interesting spectroscopic, photophysical, photochemical and electrochemical properties, which lead to potential uses in diverse areas.¹⁰ A large number of novel organic reactions have been described using ruthenium and rhodium catalysts with carbonyl, tertiary phosphines, cyclopentadienyl, and arene/dienes as supporting ligands. These ligands allow the generation of coordinatively unsaturated species and stabilize the reactive intermediates, thus favoring catalytic process.¹¹ Synthetic versatility, high catalytic performance under relatively mild reaction conditions, high selectivity makes these complexes particularly interesting for extensive research. The development and optimization of functional materials is certainly a key challenge in modern chemistry, which requires well-defined and tunable systems namely, functional units that can be specifically tailored on a chemical level. Many metal complexes containing a wide range of coordinating ligands were developed, however N-N and N-O donor ligands are found to be an outstanding candidate for this purpose.

1.1 Molecular orbital scenario for d^6 octahedral complexes:

In order to understand the nature of orbitals involved in the absorption of light linear combination of atomic orbitals (LCAO) better describes the molecular orbitals of a pseudo octahedral d^6 transition metal complex. In the octahedral d^6 complex the highest occupied molecular orbital (HOMO) is predominantly based on metal d_{π} -orbital and the lowest unoccupied molecular orbital (LUMO) is often predominantly ligand π^* orbital. The nature

and energy of the HOMO and LUMO are especially important in understanding the excited state properties of a light absorber molecule since they are the orbitals involved in the lowest energy excited state.

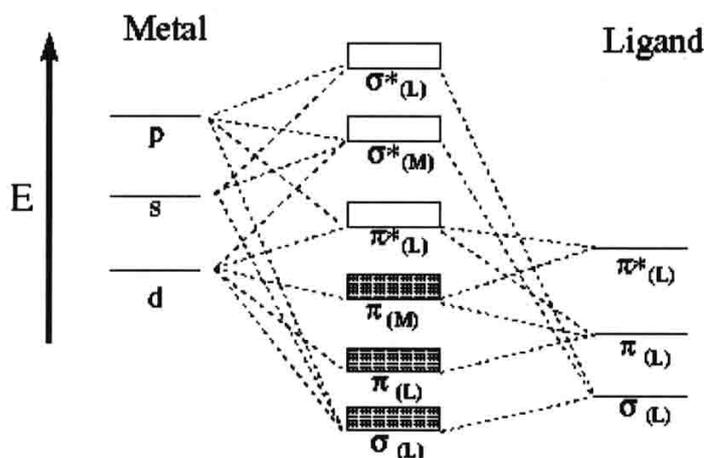


Figure 1.1 Block representation of the interacting orbitals for d^6 octahedral complexes.

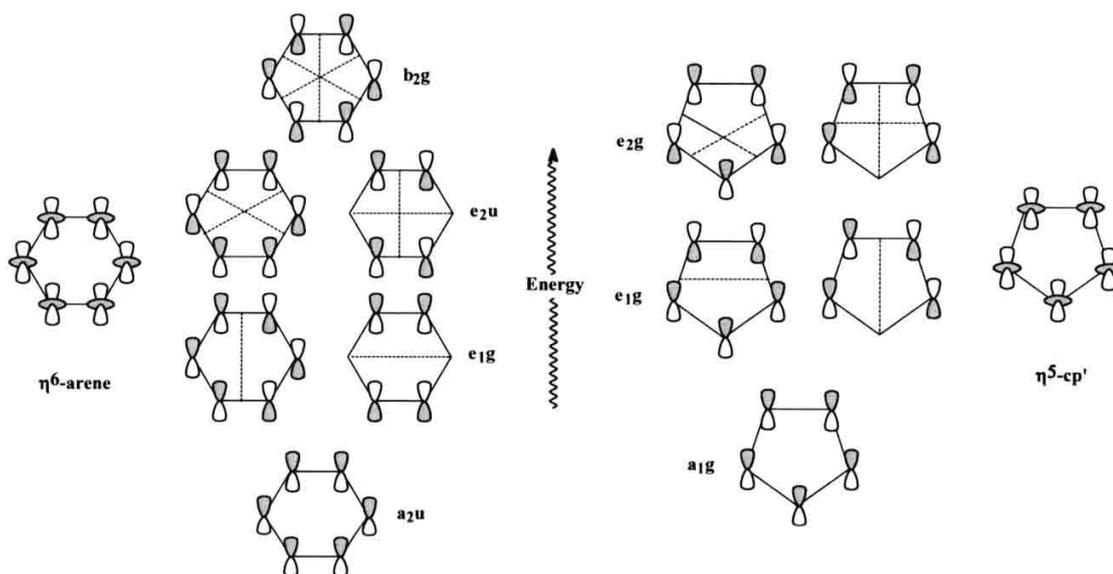


Figure 1.2. Ligand orbital picture for η^6 -arene and η^5 -cyclopentadienyl based ligands.

Each carbon center in the η^6 -arene and η^5 -cyclopentadienyl based ring has a p_z orbital perpendicular to the plane of the regular hexagon and pentagon ring, respectively (Figure 1.2). These p_z orbitals form delocalized ligand group orbitals (LGOs) that combine with atomic

orbitals (AOs) of the metal center of matching symmetries to construct molecular orbitals of corresponding organometallic π -complex. Symmetrical systems containing metal coordinated one C_5H_5 ring (or its close analogue C_5Me_5) have a principle axis of symmetry passing through the metal center and intersect the ring plane perpendicularly at the ring center with C_{5v} group. The ligand group orbitals (LGOs) of single ring interact with the various metal orbitals with similar symmetry.

1.2 Electronic behavior of d^6 octahedral complexes:

The low spin d^6 -configuration of resulting complexes obtained from the reaction of chloro-bridged dinuclear Ru(II)-arene complexes provide filled orbitals of proper symmetry on Ru(II), which interact with the low lying π^* orbitals of the ligands. Thus, one should expect a band attributable to MLCT transition $Ru(d\pi \rightarrow \pi^*)$ in the resulting complexes. Furthermore, the energy of these transitions varies with the nature of the ancillary ligands. Ruthenium(II) arene complexes with poly-pyridyl ligands exhibit desirable light absorption in the visible spectral region. Their population leads to shortened lifetimes and net ligand loss photochemistry. However, such problems does not exist with third transition series, since the CFSE is $\sim 30\%$ higher than the second, which increases the MLCT- $d-d$ energy gap.¹²

The α, α' -diimino ligands has energetically low-lying ligand π^* -orbitals, which enable a back donation of electrons from filled metal d orbitals to empty ligand orbitals. Lowering the π^* level of an acceptor ligand by incorporation of an electron withdrawing substituent can lead to a red shift of the lowest energy MLCT absorption. In order to achieve an efficient light-to-chemical conversion system, systematically ligand properties can be manipulated in the ruthenium(II) based chromophores in order to maximize $\pi-\pi^*$ and MLCT absorptivity.

An enhancement in the magnitude of the excitation coefficient for the corresponding lowest-energy bands of the complexes has been observed with increasing methylation of the cyclopentadienyl ring. In general, methylation of the cyclopentadienyl ring results in the red shift for the lowest-energy absorption band. Methylation of the benzene is known to cause a red shift in the position of $\pi-\pi^*$ band, therefore a partial contribution of the ring orbital with the long wavelength tail of the $\pi-\pi^*$ states of the complex possessing M- cp^* moiety is expected. The ruthenium complexes possessing pentamethylcyclopentadienyl have lower energy absorption bands than the corresponding bands for the indenyl group.

1.3 Luminescence behavior of d^6 octahedral complexes:

Luminescence measurements on d^6 complexes have yielded detailed information about the electronic excited states. The lowest excited configurations can be varied systematically by judicious choice of metal ions, oxidation states, and nature of the coordinated ligands, thus leading to a coherent picture of metal complex excited states. The nd^6 ($n = 3, 4, 5$) configuration has played a key role in these configurations since complexes with metal ions of these structures often have diamagnetic ground states and electronic excitation can only be achieved through one electron orbital promotion. For the complexes of elements of the second and third transition series containing strong ligands, this promotional requirement for excitation places the lowest excited states in the visible (or) near-IR region of the spectrum. The large energy gap between the lowest excited states and the ground state allows radiative process to compete with non-radiative one (quenching).

A substantial decrease in the photoefficiencies at all the emitting wavelengths has been observed upon increase in the methyl substituents on the cyclopentadienyl ligand. Complete methylation of the cyclopentadienyl ring causes a ~50% drop in photoefficiency. This reduction of photoluminescence of these methylated cyclopentadienyl derivatives are anticipated with the increased vibrational deactivation, inter- and intra-molecular non-radiative deactivation. Also, the competitive intra-molecular C-H bond activation, where the interaction of metal center to proton of the methylated cyclopentadienyl ring takes place, causes ring-slippage (η^5 to η^4) and reduces the overall photoefficiency. However, on increasing ring current, replacing cyclopentadienyl ring by indenyl produces an even greater reduction in quantum efficiency. Schiff base metal complexes are expected to exhibit higher intensity fluorescence than the free ligand, which can be correlated with an increase in structural rigidity upon coordination of metal with Schiff base to form a cyclic structure, in general a free Schiff base possesses a planar conformation.

The phenomenon of supramolecularity has distinct impact on the overall luminescent properties of the complexes. Contrasting luminescent behaviour has been expected for a similar molecular unit in solid state and solution phase. Blue shifted emission spectra have been observed for a particular complex unit in solution than that in solid state. Weak interactions are prominent and effective in solid state to assemble large superstructures, results effective red shifted emission. In solution such intermolecular interactions are weak enough to destabilize huge superstructures and causes blue shifted emission.¹³ Along with the

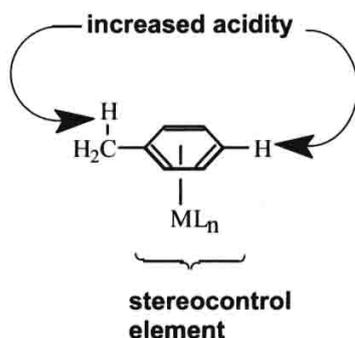
emission energy, luminescence quenching can be better correlated with the compactness or the extent of supramolecularity. In general, fluorescence quenching is observed for a less compact supramolecular assembly than that of a highly complex superstructure. Ring stacking either face-to-face or face-to-edge π - π (to some extent the C-H $\cdots\pi$) interactions generally supports fluorescence quenching.¹⁴

1.4 Electrochemical behavior of d^6 octahedral complexes:

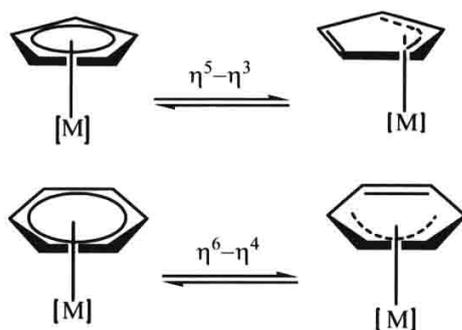
Cyclic voltammetry measures the potential at which a molecule is either oxidized or reduced. For a simple two orbital model of a molecule with one filled low-energy orbital and one empty high-energy orbital, oxidation is the transfer of an electron from the low-energy filled orbital to the electrode and reduction is the transfer of an electron from the electrode to the high-energy empty orbital of the compound in solution. In general, ruthenium(II) arene complexes with variable ligands (mono/di/polydentate) exhibits presumably a reversible metal based oxidation $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$ at $E_{\text{pa}} \sim 1.8$ V. An easier ligand centered reduction has been observed in the complexes with Ru(II)-arene moiety. Arene complexes possessing two or more fused aromatic rings are the most easily reduced species, which can be better correlated with the decrease in aromaticity with increasing size. Nitrogen donor pyridyl-azine ligands (α, α' -diimine) when incorporated into a complex exhibited an increase in the reversibility of reduction potentials by 0.6-0.8 V more positive, however free ligands have irreversible reduction potentials. The π -conjugation of these ligands are correlated with the corresponding reduction potentials, the =N-N= having higher degree of π -conjugation have lowest reduction potentials.¹⁵

1.5 Ruthenium(II) arene, Rhodium(III) cyclopentadienyl complexes and N-N & N-O donor ligands: Structural details

Arene based metal complexes have been extensively investigated in order to exploit the versatile nature of the arene as a consequence of the ease with which the arene ligand can be functionalized.¹⁶ The coordination of a metal fragment to an arene ring dramatically increases the electrophilic character of the ligand. Additionally, the presence of a transition metal center and ancillary ligands on one face of the coordinated arene can serve as a versatile stereocontrol element.

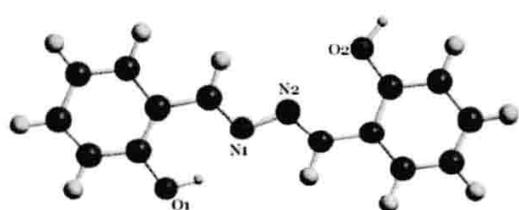


Methyl substituents of η^5 -pentamethylcyclopentadienyl and η^6 -hexamethyl benzene have considerable effect on the determination of final product. These methyl groups sterically control the formation of dinuclear complexes with a close metal-to-metal distance.¹⁷ While, the closely related η^6 -*p*-cymene ligand is sterically less demanding than hexamethylbenzene indicated that it should provide enough protection to enable the isolation of monomeric complexes. The ruthenium complexes possessing η^5 -pentamethylcyclopentadienyl and analogous η^5 -indenyl moieties are expected to be of higher reactivity with comparison to the η^5 -cyclopentadienyl analogue, due to electronic and steric factors and ring slippage nature ($\eta^5 \leftrightarrow \eta^6$), for cp* and indenyl rings, respectively.¹⁸ The introduction of five methyl groups increases the solubility of its complexes in organic solvents along with the enhancement of electron density on the metal center. Also, the steric effect will become more pronounced with each successive methyl group substitution on π -ligand, and accounts its effect on ligand displacement rates for these π -complexes.¹⁹ Upon oxidation of the metal center, the η^6 -arene ring flips to form η^4 intermediate, (a similar η^5 - η^3 ring slippage of the cyclopentadienyl ligand from coordination in certain ligand replacement or catalytic reaction) reflecting the ability of the arene ligand to donate π -electrons to the oxidized metal center such ring slippage ability provides, by creating an extra coordination site to accommodate the incoming ligand, arene complexes a potential application in field of catalysis also.²⁰

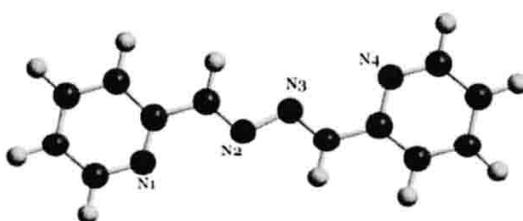


Although the steric effects of ligands on the stability or reactivity of transition metal complexes are usually difficult to quantify, however sterically bulky tertiary phosphines have pronounced effect in correlation with its cone angle. The displacement rate is decreased on the increase of cone angle of the tertiary phosphine used for π -complexes.²¹ Metal Schiff base complexes have played an important role in developing stereochemical chemistry models in transition metal coordination chemistry, mainly due to their stability, ease of preparation, and structural variability. These models are found to be an active probe for catalytic studies, due to a greater degree of flexibility on coordination to metal center.

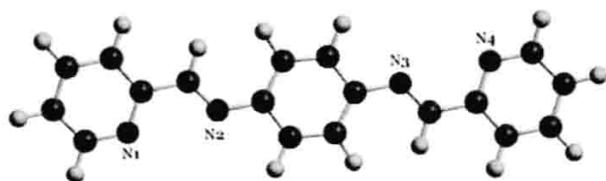
Compared with the diazine moiety in heterocyclic ring systems the N-N diazine linkages in open-chain systems with N-N single bonds are much more flexible, and literature presents a several possible mono and dinucleating coordination modes due to the flexibility of the ligand around the N-N single bond.²² Coordination and geometrical arrangements around the metal center for these ligands depends on co-ligands and reaction conditions, including steric interactions, hydrogen bonding associations, etc.. These flexible geometrical arrangements result from the ability of the systems to rotate freely about the single N-N bond of the diazine fragment. Such rotations of N-N single bond are found to affect the magnetic exchange between the metal centers in dinuclear case.²³ In combination with other donors such open chain diazine ligands can form several mono, di, tri, and tetranuclear complexes.²⁴ Because of these relative properties following ligands have been used.



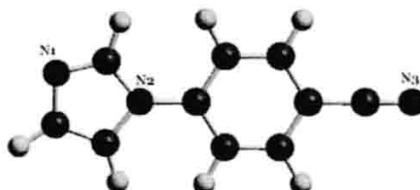
N,N'-bis(salicylidine)aldamine



N,N'-bis(picoline)aldamine



N,N'-bis(picoline)-*p*-phenylenealdamine



1-(4-cyanophenyl)imidazole

Different N-N and N-O donor ligands used