PREFACE

It has been observed that aromatic characteristic can develop in metal chelate rings due to involvement of delocalized π electron system of the ligand with the metal d-orbital. The devèlopment of aromaticity will depend upon the extent of overlap. The electron cloud on the delocalized ligand can be attracted or repelled towards or away from the metal orbitals by the substitution of the electron attracting or repelling groups on the metal ion. The nature of the adjucts may also be influenced by the delocalized π system of the metal chelate ring. Acetylacetone can be considered as a suitable ligand for investigation on the delocalization of π electron system in its metal complexes and considerable work has proved the presence of aromaticity in this series of compounds. Aromatic substitution, in this case, was possible on the middle carbon atom.[83]

The ligational characteristics of biguanide is governed not only by the σ donor capacity of nitrogen but also by the participation of dative π -bond of biguanide and monoprotonated biguanide in metal-ligand bond formation. However, biguanide differs from acetylacetone in having coordinated nitrogen atoms as sites for aromatic substitution rather than the carbon atoms. It was hence considered interesting to study the involvement of this π bond under the influence of electron attracting or electron repelling groups attached to the central metal ion. The present study is aimed at finding out qualitatively the effect of such changes in the delocalized π -system of metal-biguanides under the influence of other ligands.

As electron donor-acceptor ligands, nitric oxide and triphenylphosphine were chosen. Because of the molecular structure, nitric oxide may form nitrosyl compounds as :

(a) positive ion NO^+ with the prior transfer of the electron from the π^* orbital to the metal followed by a donation from NO^+;

(b) negative ion, NO^- , acting as a normal donor resulting from the accumulation of electron density on the π^* orbital ;

(c) coordinating group, through a donation from NO , retaining the π^* electron or as

(d) a bridging NO group just like carbon monoxide in many polynuclear carbonyls.

In contrast to amines, the donor atoms in phosphine do have empty $d\pi$ orbitals and back acceptance of electrons to these orbitals is feasible. Phosphorous in these ligands can, therefore, be visualised as a σ donor and π acceptor, the vacant 3d orbitals of the phosphorous being capable of interaction with fille nonbonding d-orbitals of the transition metal ion, resulting in the decrease of electron density on the metal d-orbital.

Attempts have been made in this thesis to prepare mixed ligand complexes having biguanide-nitric oxide and biguanide-triphenylphosphine as ligands with metal ions such as cobalt(III), iron(II) and platinum(II). The metal ions are capable of π interaction in bond formation with various ligands.

The preparation of the following compounds have been reported in this thesis.

(a) trans-$\left[Co(RBigH)_2(NO)H_2O\right]X_2$

and trans-$\left[Co(RBigH)_2(NO)Y\right]X$.

where R = H, methyl, ethyl or phenyl group

$X = ClO_4$ $\frac{1}{2}$ SO_4, CNS, Br, Cl

$Y = \cancel{H_2O}$, Cl, Br, OH, CNS.

The compounds have been characterized by their elemental analysis, conductance measurement, magnetic behaviour and spectral studies. The compounds show diamagnetism and liberate iodine from potassium iodide corresponding to oxidation state +1. The absence of nitrito and/or nitro group in the complexes was realised since 1460, 1065 and/or 1450, 1350 and 850 cm^{-1} corresponding to nitrito or nitro group were not to be found in the infrared spectrum of these compounds. In all these compounds it has been found that N - O stretch lies at 1500 to 1525 cm^{-1} indicating slight N - O double bonding and coordination of nitrosyl as NO^-. This shows that the π donor capacity of the ligand biguanide to metal ($L \rightarrow M$) is so strong that electron from the metal is transferred to antibonding π molecular orbital of nitric oxide which then coordinates as NO^-.

(b) $\left[Fe(BigH)_2(NO)_2\right](OH)_2$. This was prepared by passing nitric oxide through a suspension of bis(biguanidinium)iron(II) hydroxide in nitrogen atmosphere. Investigation of the magnetic property of the compound indicates that it has field variation magnetic susceptibility. Without ferromagnetic correction of the magnetic centres, a very high value of the effective magnetic moment results at any field strength. A value of 4.05 B.M. is obtained for this compound after ferromagnetic correction.

Intramolecular ferromagnetism is rare because of the exchange coupling through the bridging groups causing spin reduction. However, in this compound the feeble ferromagnetism can be visualized by the alignment of dipoles ($\overset{-}{NO}$ - Fe - $\overset{+}{NO}$ $\overset{-}{NO}$ - Fe - $\overset{-}{NO}$) along the z direction, the nearest neighbour iron atoms being far apart from each other due to the presence of bulky diamagnetic ligands between them along the xy plane, can not have any exchange coupling.

(c) cis-$[Pt(RBigH)(PPh_3)_2]X_2$

where R = H, methyl, ethyl, phenyl

X = OH, $\frac{1}{2}$ SO_4, Cl, NO_3, ClO_4, Br.

The compounds were characterised by elemental analysis, ionic conductance measurement and spectral studies in the infrared and ultraviolet regions. The strength of the metal biguanide bonding was realized from the shift in band positions in the ultraviolet region. The blue shift of λ_{max} values, 230 nm for biguanide to 220 nm for bis(biguanidinium)platinum(II), can be explained by taking into consideration the energy of the d-orbital of platinum(II) being above that of the π-orbital of biguanide molecule. Interaction of these two orbitals causes stabilization of π orbital and destabilization of metal d-orbitals. However, introduction of a π-acceptor ligand such as triphenylphosphine as in the present compound helps in electron withdrawal from the metal d orbital with its consequent stabilization. This brings the metal d and the ligand π orbital almost in the same energy level with no appreciable influence on each other. This has been experimentally realized as a red shift in the λ_{max} values of biguanide in $[Pt(II)(BigH)_2]^{++}$ (220 nm) to cis $[Pt(II)(BigH)(PPh_3)_2]^{++}$ (230 nm).

Finally the blue shift of λ_{max} of triphenylphosphine in this complex (from 262 nm for free PPh_3 to 258 nm for cis-$[Pt(II)(BigH)(PPh_3)_2]^{++}$) was explained by taking into consideration the flow of electrons from the metal d orbitals to the vacant d orbitals of phosphorous with the consequent destabilization of π^* orbital of triphenylphosphine.

From the above observation it can be concluded that in metal biguanide chelates the π-electron system is delocalized. This system can influence and can be influenced by the electronic systems of the adducts to attain the maximum stabilization in the metal ligand bonds.

The aromatic character of metal biguanides has been proved by the electrophilic substitution reactions such as halogenation sulphonation, and nitration on the chelate ring.[116] It has also earlier been observed that due to electron pressure from the metal biguanide rings, the electrons in metal d-orbitals tend to migrate to the antibonding orbital from which they can be easily removed to form metal complexes in unusual higher oxidation states of the metal.[119] Present study indicates that due to electron pressure the electron in the antibonding metal d-orbital may be transferred to the empty ligand orbital through the ligand under study viz. nitric oxide and triphenylphosphine which are known to act both as electron acceptors and donors.

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