CHAPTER – I

Aspects of the Platinum Metals' Complexes with Azo Ligands and the Purpose of the Present Investigation

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Abstract

In this chapter the significance of the transition metal complexes with aromatic azo(diazene) ligands with special reference to platinum group of metals is delineated. The scope and the purpose of the present work are also discussed.

I. 1 Introduction

The chemistry of aromatic azo (diazene) compounds constitutes a well-established field particularly due to their application in dye stuff [1]. Metal complexes of azo dyes and pigments enjoy special importance due their commercial application. A wide variety of metal complexes of first transition series like copper, chromium and cobalt with azo dyes have been employed commercially. The chromium and cobalt complexes are mostly used in the field of wool dye stuffs whereas copper complexes are mainly used as cotton dyestuff. Therefore, initial attention was paid only to the members of first transition series for complex formation with aromatic azo (diazene) compounds to fulfill the requirements of dye industry. Subsequently, the studies on the structure and bonding of the first transition metal complexes with azo ligands provided interesting results [2]. These results opened up the new avenue of studies on the azo complexes of second and third transition metal ions.

First transition metal complexes with azo ligands

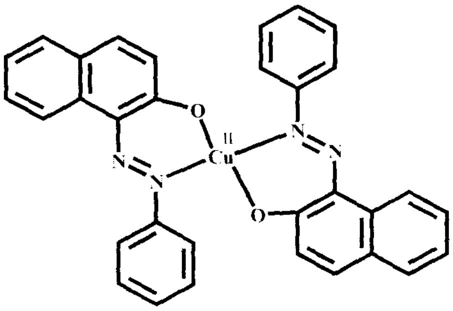
First transition metal complexes with aromatic azo (diazene) compounds may be classified into following groups.

Bidentate systems

Metal complexes with bidentate azo ligands find their application mainly in the field of pigment rather than dyestuff. The first report of transition metal compound with bidentate azo ligand was published [3] by Carberti and Peco in 1893. They obtained brown compound from the reaction of *p*-nitrobenzene-azo-β-naphthol with copper salts. The reactions of bidentate azo ligands like *o*-hydroxy and *o*-amino azo arenes with copper(II), nickel(II) and cobalt(II) were studied by a number of workers [4-8].

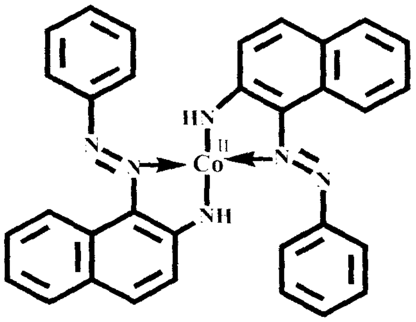
The classical work [9] by Drew *et. al.* finally established that *o*-hydroxy and *o*- amino azo compounds formed complexes having 2:1 stoichiometry with copper(II) and nickel(II).

The X-ray crystal structure of copper complex of benzeneazo-β-naphthol was reported by Jarvis [10]. The divalent copper in the complex (**1**) is centrosymm -etrically disposed with two oxygen atoms and two β-nitrogen atoms of the azo groups forming a square.



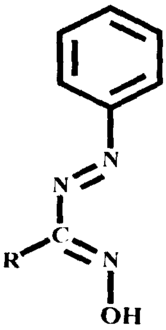
(**1**)

The cobalt complexes with *o*-hydroxy azo compounds were extensively studied by Price [11]. Benzeneazo-β-naphthol (HL) reacts with cobalt(II) acetate to form complex $[CoL_2]$. The magnetic susceptibility of $[CoL_2]$ suggests tetrahedral geometry of the complex. Neutral diamagnetic $[CoL_3]$ complex was isolated from the reaction of sodium tris(carbonato)cobaltate (III) with benzeneazo-β-naphthol (HL) [12]. Benzeneazo-β-naphylamine also form complex with cobalt(II) and the structure of the complex, proposed by Price [11], is shown below (**2**).



(**2**)

Another important group of bidentate azo ligands is arylazooximes (HL) (**3**), which is obtained by nitrosation of arylhydrazones of aldehydes by *n*-amyl nitrite [13]. Hunter and Roberts first reported cobalt(III) chelates of arylazooximes [14]. A few nickel(II) complexes were subsequently isolated by Malatesta et al.[15]. Arylazooximes which undergo extensive intermolecular hydrogen bonding can apparently exist in geometrically isomeric forms [16].



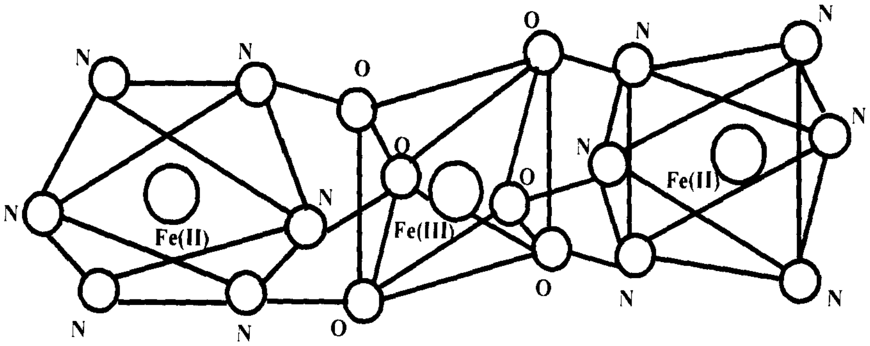
(3)

First transition metal complexes with arylazooximes exhibit interesting structural features as well as electron transfer properties.

Arylazooximes react with cobalt(II) or cobalt(III) salts in presence of excess amines to produce very stable tris(aryloximato)cobalt(III) complexes [17].

Infrared data suggest the existence of five-membered chelate rings in these complexes. The proton magnetic resonance spectra of the complexes conclusively demonstrate *trans* configuration of the tris chelates. The sterically unfavorable *cis* isomer could not be identified.

The reaction of arylazooximes (HL) with iron(II) perchlorate in ethanol affords complex $[Fe_3(L)_6]ClO_4$ **(4)** [18-20]. The trinuclear complex cation $[Fe_3(L)_6]^+$ contain two iron(II) centers and one iron(III) as central atom. The two terminal iron(II) atoms are held in the facial tris chelate environment of azo and oxime nitrogen atoms. The central iron(III) atom is octahedrally surrounded by six oximato oxygen atoms. Each oximato function acts as a bridge between iron(III) and iron(II) atoms.



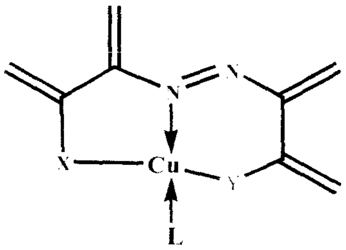
(4)

View of the coordination spheres of the three iron atoms in $[Fe_3(L)_6]^+$

The copper(II) complexes of arylazooximes (HL) were synthesized by chelation reactions between copper(II) acetate and arylazooximes in methanolic solution [21]. The empirical formula of the complexes corresponds to $Cu(L)_2$. They are uniformly diamagnetic in the solid state as well as benzene solution. They exhibit well-resolved ^1H NMR bands in chloroform solution. The cryscopically determined molecular weight of the complex shows *dimeric* nature i.e. $Cu_2(L)_4$ of the complexes.

Terdentate systems

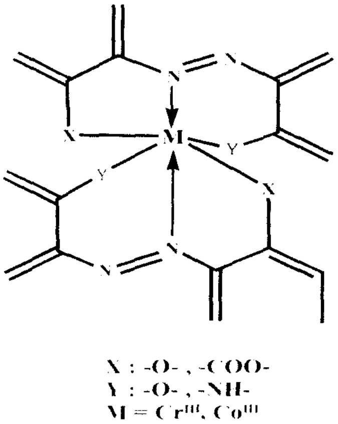
The important terdentate azo ligands are o,o′-dihydroxyazo, o-carboxy-o′-hydroxyazo and o-hydroxy-o′-aminoazo arenes. The structures of the copper(II) complexes (**5**) are shown below.



X : -O- , -COO-
Y : -O- , -NH-
L : H_2O

(**5**)

Chromium(III) and cobalt (III) with terdentate ligands form $[ML_2]$ complexes as shown in (**6**) [22]. The X-ray crystal structure of chromium(III) complex with o,o′-dihydroxyazo arene was reported [23]. The structure of chromium(III) complex of o-carboxy-o′-hydroxyazo dye was determined by X-ray crystallography [24].

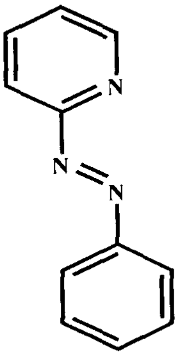


X : -O- , -COO-
Y : -O- , -NH-
M = Cr^{III}, Co^{III}

(**6**)

Azo ligands having hetrocyclic nitrogen atom *ortho* to diazene group

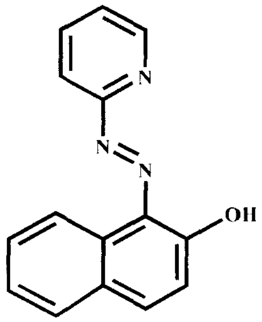
2-(Phenylazo)pyridine (**7**) is an important bidentate neutral ligand and well known for its π acidity [25].



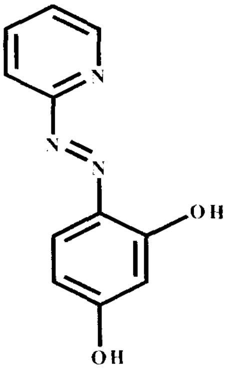
(7)

Detailed studies have been done on its nickel (II) and iron(II) complexes [26]. Both copper(II) and copper(I) react with 2-(phenylazo)pyridine (L) and yield cationic bisligand complexes grossly planar $[CuL_2](ClO_4)_2$ and tetrahedral $[CuL_2](ClO_4)$ respectively [27]. The d(Cu)-n*(L) back-bonding is reflected from the large shift of N=N stretch to lower frequency from the free-ligand.

Terdentate o-hydroxyazo compounds having hetrocyclic nitrogen atom *ortho* to diazene group and their metal complexes find application in dyeing of metal containing poly-α-olefins. Pyridineazo-β-naphthol (PAN) (**8**) and pyridineazoresorcinol (PAR) (**9**) have been extensively used in spectrophotometric and titrimetric determination of metal ions[28-31]. They have also been utilized in the separation of metal ions by solvent extraction techniques. Fernando *et. al.* reported the crystal structure of the copper complex of pyridineazo-β-naphthol, $[Cu(PAN)\ H_2O]\ ClO_4$. The molecule is nearly planar [32].



(8)



(9)

Platinum metals' complexes with azo ligands

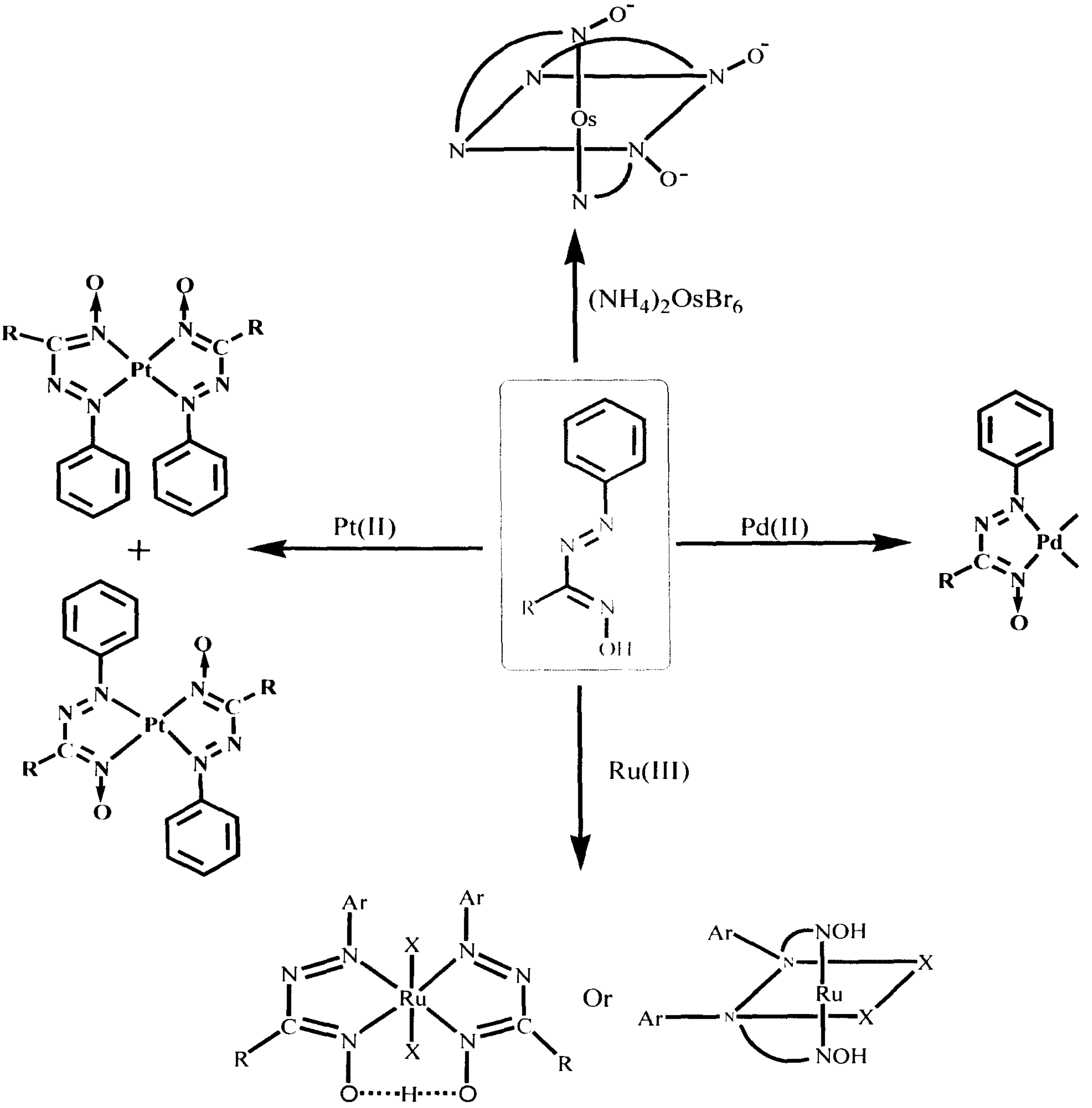
The platinum metals' complexes of several diazene ligands has received considerable attention largely because of the interesting spectroscopic and redox properties exhibited by them [33].

Bidentate systems

One of the most important azo ligand in this regard is the arylazo oximes (**3**). Initiated by Chakravorty *et al.*, extensive studies were carried out on chemistry of arylazo oximes of platinum metals (Scheme I.1) [33a].

Palladium(II) reacts with arylazo oximes and forms palladium(II) arylazo oximates that undergo selective bond cleavage reactions and equilibria [34-37].

Platinum(II), on the other hand, forms bis chelate complexes with arylazo oximes []. Both *cis*- and *trans*- platinum(II) bis chelate complexes have been characterized. The *cis* isomer undergoes an interesting oxidation leading to the formation of $[Pt(L)_2]^+$ (L= arylazo oxime) [38, 39].



Scheme I.1

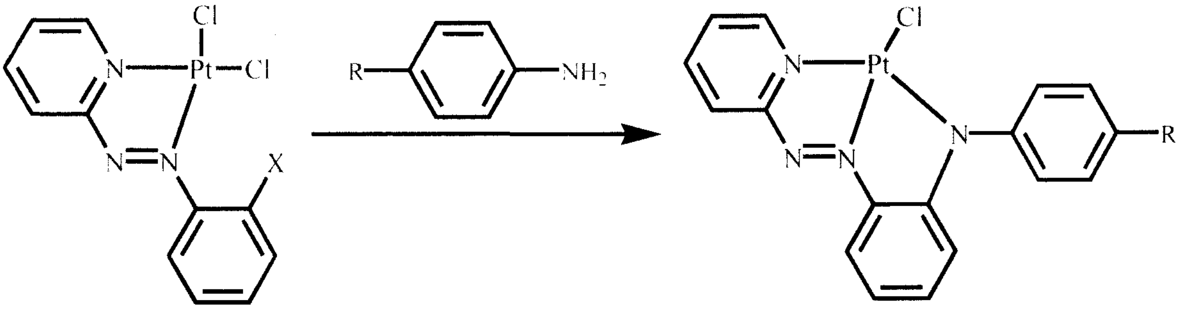
Rhodium(III) forms tris chelate complexes with arylazo oximes. Both facial (*cis*) and meridional (*trans*) isomers have been identified in this case [40]. Interestingly, the two isomers show marked differences in their redox behaviour.

Ruthenium azo oxime chemistry is rich and extensively studied [41-46]. Both ruthenium(II) and ruthenium(III) complexes have been prepared and structurally characterized. The octahedral ruthenium complexes are invariably characterized by extensive $t_2(Ru) \rightarrow \pi^*(azo)$ charge transfer [44].

The chemistry of osmium is relatively less explored in this regard. With arylazo oximes, osmium forms facial OsL_3^- (L= arylazo oxime) [47]. Trinuclear adducts of OsL_3^- with divalent first-row transition metals have also been synthesized.

Interesting patterns of structure and reactivity in platinum metals' complexes have emerged from another group of azo ligand, *viz.*, 2-(arylazo)pyridines (AAP) (X). (Phenylazo)pyridines reacts with $PdCl_2$ and forms dichloro(phenylazo)palladium(II). The pendent phenyl group of this complex undergoes aromatic hydroxylation in presence of Ag(I) salts [48].

Platinum(II) reacts with 2-(arylazo)pyridines and forms complexes of the type $[PtCl_2(AAP)]$ [49]. The pendent aryl ring of the coordinated AAP ligand has been shown to undergo selective *ortho*-amination to form a monochloro platinum(II) complex (Scheme I.2) [49]. Recently an interesting reaction between $[PtCl_2(AAP)]$ and 2-alkylthioanilines has been reported where cleavage of S-C(sp^3) bond of 2-alkylthioanilines is noted ultimately resulting in the formation of a mixed chelate complex [50].

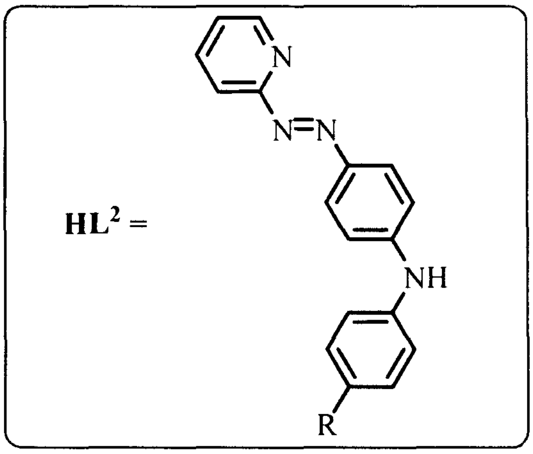


Scheme I.2

Ruthenium complexes of 2-(arylazo)pyridines deserves special mention due to their interesting electronic and redox properties [51-53]. In general, RuX_3 reacts with AAP and forms dihalo chelate complexes of the type $[RuX_2(AAP)_2]$ (X=Cl, Br, I) [52]. However, ruthenium(II) complexes of the type $[Ru(AAP)_3]^{2+}$ have also been prepared

[51]. Due to the excellent π-acceptor capacity of the ligands, these Ru(II) complexes are characterized by strong metal-to-ligand back-bonding [51-53]. Moreover, $[Ru(AAP)_3]^{2+}$ undergoes regioselective para-amination at all the coordinated ligands (Scheme I.3) [54].

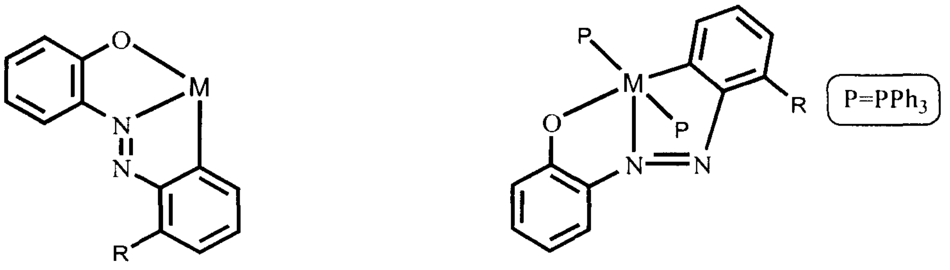
$$[Ru(AAP)_3]^{2+} \xrightarrow{ArNH_2} [Ru(HL^2)_3]^{2+}$$



Scheme I.3

Terdentate systems

Platinum metals' complexes of several terdentate azo ligands are known in the literature. (Arylazo)phenols and related ligands have been thoroughly examined in this regard. Although 2-(arylazo)phenols usually bind to the platinum metals' as bidentate N,O-donors forming either a six-membered [55-59] or a five-membered chelate rings [60], in several cases, C-H activation form an *ortho* position of the pendent aryl ring has been observed [61]. Platinum metals' complexes of the (arylazo)phenol ligands have been shown in Scheme I.4 [62-65].



M= Pd(II). Pt(II) **M= Rh(III). Rh(III), Ru(III)**

Scheme I.4

Alkyl 2-(arylazo)phenyl thioethers having terdentate monoanionic (C,N,S) donor set have also been utilized and extensively studied [66-68].

I.2 Purpose of the present work

The six platinum group metals *viz* ruthenium, rhodium, palladium, osmium, iridium, and platinum have tendency to occur together in the same mineral deposits and have similar physical and chemical properties. They are are well known for their softness. The most important aspect of platinum metals chemistry is the outstanding catalytic properties of their coordination complxes. Therefore, synthesis and characterization of new platinum metals complexes are highly desirable.

Our main objective in this thesis is to develop some newer aspects of the chemistry of platinum metals with azo ligand frame in conjunction with a *soft* sulfur donor along with a naphtholato function. The ligands are terdentate and possess O, N, S donor set While we will attempt to synthesize new complexes, structural diversity will be one of the core issues.

We wish to adopt the following strategy:

1. The choice of platinum group of metals to be restricted to ruthenium, rhodium, palladium, iridium, and platinum except osminum. Preference would be given to lower valent *soft* metal ions.

2. The azo (diazene) group is well known to bind different metal ions and also for its *softness*. The azo (diazene) function in the ligand frame would be supplemented by one *soft* thioether donor along with a naphtholic group.

3. The behavioural pattern of the terdentate ligand frame towards both low-valent and high valent platinum metals would be examined.

4. Two types of carbon-sulphur bonds viz $-S-C(sp^3)$ and $-S-C(sp^2)$ are present in the terdentate group of ligands with O,N,S donor set. Reports on C-S bond scission on metal centers, particularly platinum metals, are available in the literature. Therefore, the reactivity of the terdentate group of ligands with O,N,S donor set with platinum metals would be closely monitored with a focus on metal assisted C-S bond cleavage.

5. The characterization of new complexes would be done using different spectroscopic techniques and single crystal X-ray diffraction method.

6. The electron transfer properties of the metal complexes would be studied in non-aqueous media by cyclic voltammetry.
7. The electronic structure of the representative complexes would be calculated using Time dependent density function theory (TD-DFT). The simulated electronic spectra would be compared with those, which are experimentally observed.

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