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PHOTOCHEMISTRY OF SOME COBALT(III)-AMINE COMPLEXES: EFFECT OF ENVIRONMENT ON THE REACTIONS OF EXCITED STATE*

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Photochemistry of cobalt(III)-amine complexes in different media has been reviewed. In aqueous medium, the product formation depends on the wavelength of irradiation. In mixed solvents, viscosity does not affect the redox quantum yield. Photochemistry of cobalt(III)-amines in non-aqueous media is interesting. Cobalt(II) complexes formed during photolysis reacts with dissolved oxygen in the medium to form mononuclear superoxo(I), μ-dinuclear superoxo(II) and μ-peroxo(III) complexes. These oxygenation reactions have been studied by flash photolysis method.

Key Words : **Cobalt(III)-Amine Complexes; Photochemistry**

INTRODUCTION

THE excited state properties of a wide variety of cobalt(III) complexes have been investigated in the last three decades.[1,2] The ground state reactions of these d^6 ion coordination compounds in aqueous and non-aqueous solutions have been understood in greater detail than the excited state reactions.[3,4] Cobalt(III) complexes are of low spin type and inert and therefore can be studied in aqueous solutions conveniently. Except the cyanide coordinated complexes, cobalt(III) systems do not emit[5] and hence the physical properties of the excited states such as lifetime, distortion from the ground state and the nature of the various deactivation processes of the excited state could not be determined. In the absence of emission from the complexes the excited states have beed studied using indirect techniques such as photosensitization.[6] There are several studies reporting the photochemical behaviour of cobalt(III)-amine complexes in different solvent mixture, in micellar media and in microheterogeneous media as well.[7] The solvent medium appears to have significant influence on the photophysical pathways of the excited states and photochemical processes.[8]

SPECTROSCOPY OF COBALT(III) COMPLEXES

Cabalt(III) complexes with octahedral micro symmetry show low intensity Laporte forbidden ligand field bands and high intensity charge transfer bands.[9] These

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assignments are shown in the energy level diagram for a cobalt(III) complex in Fig. 1. While cobalt(III)-amine complexes do not show any optical emission from the excited states, $Co(CN)_6^{3-}$ ion shows luminescence.[10] Photochemistry of the amine complexes differ considerably from that of the cyano complexes. Existence of the triplet excited states has been suggested for a few complexes. However, the triplet states do not show emission and the reactivity of these states could not be ascertained. The charge-transfer bands are assigned to be ligand to metal type[11] and this assignment is supported, particularly in the case of the amine complexes, by the fact that the charge-transfer band maximum shifts to longer wavelengths if the coordinated ligand to the cobalt(III) centre is more easily oxidisable[12] as shown in Fig. 2. The ligand field bands do not display changes due to different solvent environment while the charge-transfer bands do shift in different solvents.[13] The two ligand field bands are broad and the transitions involve electron density in antibonding levels populated. The quantum yield for aquation and redox reactions of a number of complexes are given in Table I. From the table it may be seen that the ligand field photochemistry is complicated by the occurrence of redox reactions. It appears that the quantum yields for photoaquation reactions are wavelength-dependent.

In cases such as $Co(NH_3)_5\ NO_2^{2+}$, $Co(en)_2\ (NO_2)_2^+$ [14] and $Co(EDTA)\ NO_2^-$ [15] a new photochemical reaction mode is observed namely linkage isomerization of the NO_2^- ligand to form a $Co^{(III)}$—ONO product.

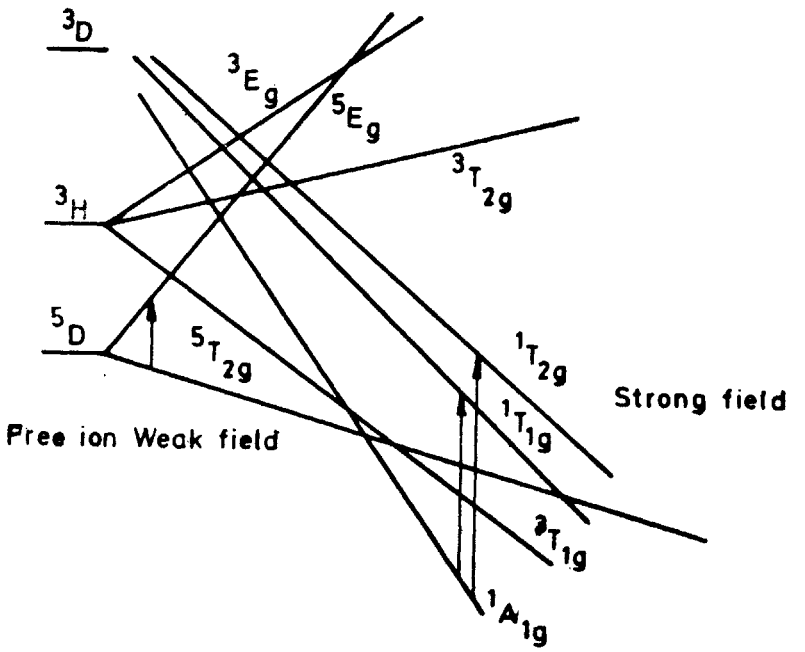

FIG 1 Energy level diagram for Co(III).

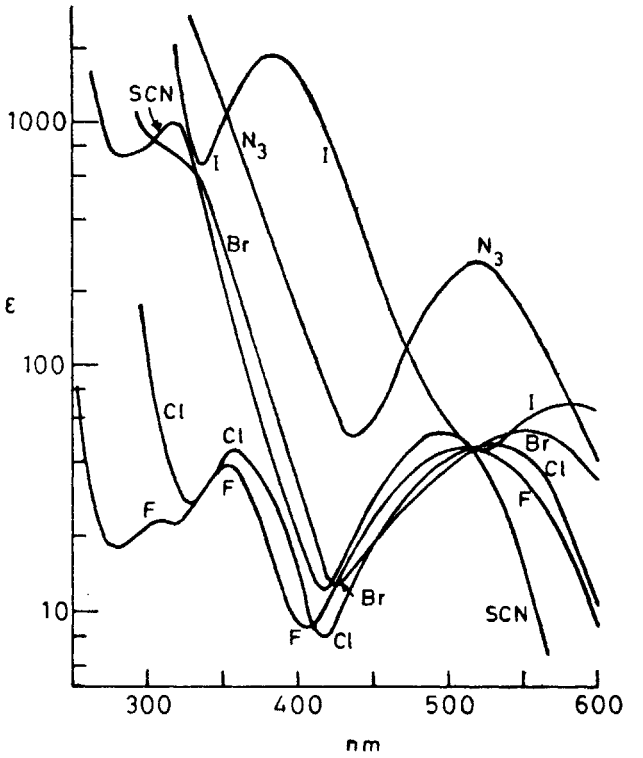

FIG 2 Absorption spectra of $Co(NH_3)_5 X^{2+}$ complexes.

TABLE I

Photochemical reactions of cobalt(III) complexes

Complex	Wavelength of irradiation	ϕ_x	ϕ_{NH3}	ϕ_{redox}
$Co(NH_3)_5 Cl^{2+}$ [a] [b] [c]	254	—	—	0.17
	370	0.0011	trace	trace
	488	17×10^{-3}	5×10^{-3}	10^{-4}
$Co(NH_3)_5 Br^{2+}$	254	trace	trace	0.33
	410	0.069	—	0.071
	550	1.4×10^{-3}	—	10^{-4}
$Co(NH_3)_5 NCS^{2+}$ [d]	496	—	$< 10^{-4}$	$< 10^{-4}$
$Co(NH_3)_5 N_3^{2+}$	254	—	—	0.2
	520	$< 10^{-3}$	0.27	$< 3 \times 10^{-4}$
Co(HEDTA) Cl^- [e]	254	—	—	0.09
	400	0.04	—	0.08
Co(HEDTA) Br^- [e]	350	0.09	—	0.035

a. Endicott and Hoffman.[16]
b. Adamson.[19]
c. Pribush *et al.*[22]
d. Adamson and sporer.[23]
e. Natarajan and Endicott.[15]

Mechanism of the Redox Photochemistry of Cobalt(III)-Amine Complexes in Aqueous Solution

Cobalt(III) complexes on excitation in the charge-transfer bands produce cobalt(II) and oxidised ligand.

$$Co(NH_3)_5\,X^{2+} \xrightarrow[H^+,H_2O]{h\nu} Co(H_2O)_6^{2+} + \text{Products}$$

Among the coordinated ligands the oxidised ligand is the one which is more easily oxidised. In the acidopentammine cobalt(III) complexes, the acido group is invariably oxidised and in the case of chloro and bromo complexes in the flash photolysis experiments Cl_2^- or Br_2^- transients have been observed.[16] In aqueous solutions, the cobalt(II) complexes produced during photolysis rapidly get aquated due to the labile nature of the cobalt(II) species to produce eventually hexaaquocobalt(II) complex. Lilie and Simie[17] have estimated that the photolysis of $Co(NH_3)_5X^{3+}$ complex leads to the release of three ammonia ligands from the photoproduced $Co(NH_3)_5^{2+}$ in a few microseconds.

A general mechanism for the photoredox reaction of cobalt(III) complexes was proposed by Adamson[19] which involves a radical pair with varying amounts of energy depending upon the energy of the photon as shown in the scheme

$$Co(NH_3)_5\,X^{2+} \overset{h\nu}{\rightleftharpoons} [Co^{II}(NH_3)_5.X] \longrightarrow Co^{II}(NH_3)_5 + {}^{\cdot}X$$

The radical pair prefers to go back to the starting material if the kinetic energy of the radicals is too low to effect separation into bulk solvent. Accordingly, the quantum yield was predicted to vary depending upon the wavelength of excitation of the molecule. In several cases, such a dependence on the quantum yield upon the energy of the irradiated light was observed. Since the absorption bands which were irradiated contain different bands overlapping, it is difficult to attribute the variation of quantum yield with the excitation wavelength to the geminate recombination mechanism. It is also to be mentioned that in the redox process a low spin cobalt (III) complex is converted to a high spin cobalt(II) complex and the spin multiplicity of the cobalt(II) complex in the radical pair is not known. On thermodynamic grounds the oxidation of the cobalt(II)-amine by the oxidised radical in the geminate pair should be feasible. Langford[20] has recently interpreted the dependence of redox quantum yields on the wavelength of irradiation. Accordingly, monotonic decline of the redox or substitution yield for a reaction initiated by a homolytic cleavage as wavelength increases in terms of rapid redistribution of energy into all vibrational modes of a complex. Excess reaction at shorter wavelength indicates some cage escape prior to full vibrational relaxation coupled to solvent relaxation. The full wavelength dependence of the yields of the chloropentammine cobalt(III) ion was recently investigated.[21] The decline of both NH_3 and Cl^- yields across the singlet manifold suggests an intersystem crossing competing with vibrational relaxation in the singlet. It is observed that the sulphinato complex $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$ undergoes photochemical linkage isomerization.[22]

PHOTOCHEMICAL REACTIONS OF COBALT(III) COMPLEXES IN MIXED SOLVENT SYSTEMS

Scandola *et al.*[31] have investigated the photochemical behaviour of cobalt(III)-amines in water-glycerol mixtures and observed that the quantum yield for cobalt (II) decreases in that medium. Irradiation of $Co(NH_3)_5 (NO_2)^{2+}$ in glycerol-water medium gives cobalt(II) and linkage isomer, $Co(NH_3)_5 ONO^{2+}$. The quantum yield for cobalt(II) decreases at higher glycerol concentration, while the quantum yield for the linkage isomer is enhanced. However, the total quantum yield for the products formation remains the same at different ratios of water-glycerol as solvent. Endicott *et al.* have investigated in detail the photoredox reactions of several acidopentammine cobalt(III) complexes[23] and observed contrasting behaviour for different systems. Heavy atom effect has been observed in certain cases. Photochemistry of $Co(NH_3)_5 (NO_2)^{2+}$ ion has been investigated in aqueous solutions containing macromolecules.[24] The viscosity of the solutions were very high and in these highly viscous solutions the quantum yields for the redox process and the formation of the linkage isomer were found to be the same[23] as those in aqueous solutions without the high polymer present. Photochemical behaviour of $Co(NH_3)_5 (NO_2)^{2+}$ and $Co(NH_3)_5 N_3^{2+}$ has been investigated in aqueous medium containing added hydroxylic solvents[24] to examine the role of solvent viscosity in determining the extent of radical breakdown. The results are shown in Fig. 3. It was conclud-

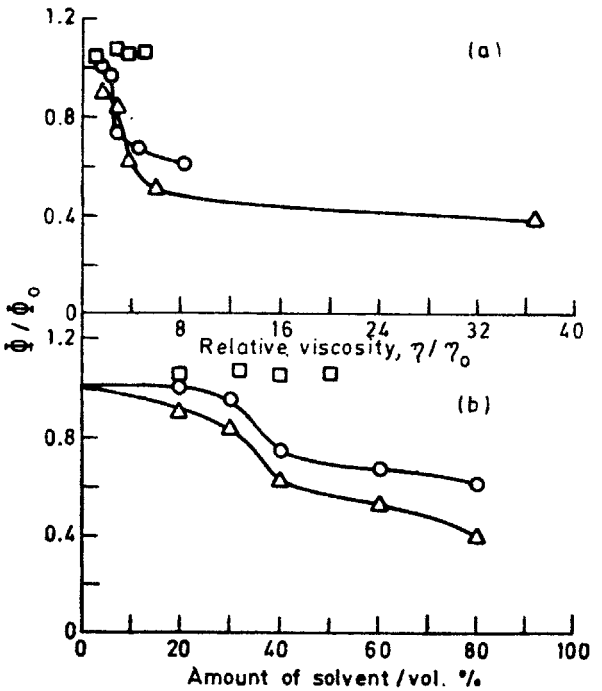

FIG 3 Quantum yields of Co^{II} on irradiation of $Co(NH_3)_5 N_3^{2+}$ in solution (ϕ_0) and in solvent mixtures (ϕ) : (Δ) water-glycerol; (○) water-ethylene glycol; (□) water-ethanol-cyclohexanol.

ed that a more specific role exists for the added solvent. The effect of adding synthetic polymers to give high viscosities again leaves the redox quantum yields unchanged, which may simply reflect the heterogeneous nature of the polymer solutions.[25]

In order to investigate more closely the effect of environment on the photoredox reactions of cobalt(III)-amine complexes attempts have been made to have polymeric ligands coordinated to the cobalt(III) centre and determine the photochemical behaviour.[25,26] Complexes of the type $Co(en)_2$ (PVP)X (X = Cl, Br), (PVP = poly(4-vinylpyridine)) and $Co(en)_2$ (PAA)X, (PAA = polyacrylic acid) have been synthesized and the quantum yields have been determined for the cobalt (II) formation. The results are shown in Table II along with the quantum yields for the monomeric complexes. The results indicate that the quantum yield decreases invariantly for the complexes with macromolecular ligands. With more number of cobalt(III) centres present in a given macromolecular chain the quantum yield increases which is attributed to the more exposure of the complex ion to the aqueous environment.

TABLE II

Quantum yield of cobalt(II) formation from monomeric and polymer cobalt(III) complexes, excitation wavelength 315nm

Complex	Percentage of complex	$\phi_{Co^{2+}}$
cis-$[Co(en)_2$ (py) Cl$]^{2+}$	—	0.0124
	42.30	0.0130
cis-$[Co(en)_2$ (PVP) Cl$]^{2+}$	9.95	< 0.003
	12.20	< 0.003
	16.44	0.0078
	37.44	0.0093
cis-$[Co(en)_2$ (py) Br$]^{2+}$	—	0.0620
	30.00	0.0670
cis-$[Co(en)_2$ (PVP) Br$]^{2+}$	2.65	0.0160
	4.00	0.0210
	5.60	0.0224
	6.70	0.0230
	19.20	0.0252

PHOTOREDOX REACTIONS OF COBALT(III) COMPLEXES IN NON-AQUEOUS SOLVENTS

Although there has been some studies on the thermal reactions of cobalt(III) complexes in non-aqueous solvents, not much work is reported on the photochemical behaviour of these complexes in non-aqueous solvents. In order to investigate the role of neat non-aqueous solvents photochemistry of cobalt(III)-amine complexes has been investigated in acetonitrile, ethanol and methanol. It was observed that the photolysis of cobalt(III)-amine using xenon lamp produces cobalt(II) complexes

which react with dissolved oxygen.[27-29] However, in aqueous solution no such reaction is observed presumably because the cobalt(II) produced photochemically is very labile and is converted rapidly to cobalt(II) aquo ion before it could react with oxygen. This approach provides a means to investigate the reactions of oxygen with cobalt(II)-amine complexes.

In the case of *cis*-$Co(pn)_2(NO_2)_2^+$ [29] ion dissolved in acetonitrile shows the transients given in Fig. 4, on flash photolysis of the complex. The transients correspond to the reactions given in the scheme.

$$cis\text{-}[Co(pn)_2(NO_2)_2]^+ \xrightarrow{h\nu} Co(pn)_2NO_2 + \cdot NH_2$$

$$Co(pn)_2(NO_2)^+ + O_2 \longrightarrow \underset{\mathbf{I}}{Co(pn)_2(NO_2)O_2^+}$$

$$Co(pn)_2(NO_2)^+O_2 + cis\text{-}[Co(pn)_2NO_2]^+ \longrightarrow \underset{\mathbf{II}}{[(NO_2)(pn)Co(O_2^-)Co(pn)_2}$$

$$(NO_2)_2]^{2+} \longrightarrow \underset{\mathbf{III}}{[(NO_2)(pn)_2Co(O_2^{2-})Co(pn)_2}$$

$$NO_2]^{2+} + NO_2$$

Steady photolysis of the complex in acetonitrile in air-equilibrated solutions produces μ-peroxo dinuclear complex. A number of these complexes have been studied in different solvents and the results are given in Table III.

Reactions of Photoproduced Cobalt(II) Complexes with Molecular Oxygen

The kinetics of the oxygenation of cobalt(II)-amine complexes has been investigated extensively using the stopped-flow method.[30] In these studies cobalt(II)-amines

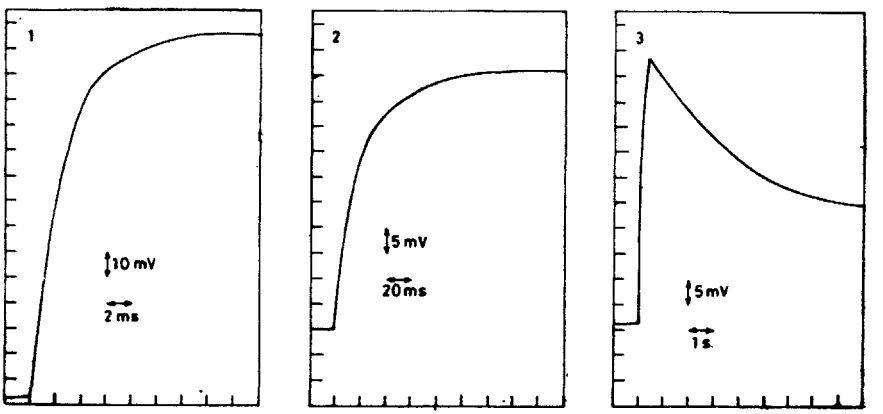

Fig 4 1. Transient growth of absorption at 400nm (I).
2. Transient growth of absorption at 700nm (II).
3. Transient decay of absorption at 700nm (III).

TABLE III

Steady photolysis of cobalt(III)-amines in CH_3CN and CH_3OH

Complex	λ_{max} nm	
	CH_3CN	CH_3OH
cis-[Co(*pn*)$_2$ (NO_2)$_2$] ClO_4	342	343
	430 (sh)	430 (sh)
trans-[Co(*pn*)$_2$ (NO_2)$_2$] ClO_4	327	323
	430 (sh)	425 (sh)
trans [Co(*pn*)$_2$ Cl_2] ClO_4	305	305
	380 (sh)	390 (sh)
	460	460
	590	582
trans-[Co(*tn*)$_2$ (NO_2)$_2$] ClO_4	352	350
	440 (sh)	430 (sh)
trans-[Co(*tn*)$_2$ NO_2Cl] ClO_4	320	310
	385 (sh)	385 (sh)
	480	475
	630	632
[Co(*dien*) (NO_2)$_3$]	337	337
	430 (sh)	430 (sh)
[Co(*dien*) (*en*) NO_2] (ClO_4)$_2$	340	330
	430 (sh)	425 (sh)
[Co(*dien*) (*pn*) NO_2] (ClO_4)$_2$	315	324
	440 (sh)	450 (sh)

were mixed with oxygen where the μ-peroxo dinuclear complex is formed as the final product. Often, the nature of the coordination environment of the cobalt(II) complex is not well known and the data are fitted to a mechanistic scheme and details of the different steps involved in the reaction are not well understood. There is a large volume of literature on the thermodynamic data on the oxygenation of cobalt(II) complexes.[30]

We have developed a new approach for investigating the oxygenation reaction. The lability of cobalt(II) complexes is less in non-aqueous solvents with low dielectric constant. Photolysis of cobalt(III)-amine complexes in aqueous solutions produces cobalt(II) complex which loses the coordinated amines before it reacts with oxygen. Since cobalt(II) aquo complexes do not react with molecular oxygen, no oxygenation reaction is observed in aqueous solution. However, photolysis of cobalt(III)-amines in acetonitrile or alcohol produces cobalt(II) complex which reacts quantitatively with dissolved oxygen. In these cases it is fairly certain that cobalt(II) complex produced photochemically retains the coordinated ligands as in the parent complex except one of the ligands which got oxidised. Therefore, flash photolysis method offers the convenient way to study the oxygenation reaction in details. Since excess cobalt(III)-amine complex is present in the medium there is no

immediate reaction to produce the μ-peroxo dinuclear cobalt(III) complex. In a typical case the transients representing different steps are shown in the scheme for the oxygenation reaction. The mononuclear superoxo complex which is not very stable reacts with the starting material to form the μ-superoxo dimer. Since the reactions are taking place at different time scale it has been possible to monitor different steps in the flash photolysis investigation. The rate constants determined for the different oxygenation reactions are shown in Table IV for a variety of cobalt(III)-amine systems.

TABLE IV

Flash photolysis of cobalt(III)-amines in CH_3CN and CH_3OH
Monitoring wavelength = 400nm and 700nm

Complex	CH_3CN		MeOH	
	400nm growth k_{obs}, s^{-1}	700nm decay k, s^{-1}	400nm growth k_{obs}, s^{-1}	700nm decay k, s^{-1}
cis-[Co(*pn*)$_2$ (NO_2)$_2$] ClO_4	480	2.05	42.6	0.56
trans-[Co(*pn*)$_2$ (NO_2)$_2$] ClO_4	300	0.11	30.1	0.39
trans-[Co(*pn*)$_2$ Cl_2] ClO_4	408	0.38	—	—
trans-[Co(*tn*)$_2$ (NO_2)$_2$] ClO_4	72	1.41	8.4	0.39
trans-[Co(*tn*)$_2$ (NO_2) Cl] ClO_4	146	0.90	0.3	0.99
trans-[Co(*tn*)$_2$ Cl_2] ClO_4	488	0.35	—	—
[Co(*dien*) (NO_2)$_3$]	50	0.36	0.53	0.98
[Co(*dien*) (*en*) NO_2] (ClO_4)$_2$	588	0.15	66.2	0.23
[Co(*dien*) (*pn*) NO_2] (ClO_4)$_2$	134	1.47	289.0	0.52

PHOTOREACTIVE STATES OF COBALT(III) COMPLEXES

Reactions of cobalt(III) complexes induced by light appear to take place from at least two different states. The *d-d* band excitation almost quantitatively leads to the ground state by non-radiative pathway while the charge-transfer excitation of the complexes leads to redox reactions to some extent. The linkage isomerisation brought about by light is due to the charge-transfer excitation of the complex. It also appears that the charge-transfer excitation does not produce considerable photoaquation indicating that the deactivation of the charge-transfer state is not taking place through the *d-d* state which undergoes photoaquation. Regarding the formation of products from the charge-transfer excited state apparently the quantum yields for product formation varies with the environment of the excited state implying the solvent control on the product formation. In particular in all the redox reactions induced by light, the role of solvent in the separation of products is important. It is well known that in many excited state electron transfer reactions, eventhough electron transfer occurs between the excited donor and acceptor, separation of the products into the bulk solvent does not happen in less polar solvents; recombination in the cage occurs giving back the starting materials.

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