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# Stabilities of Ternary Complexes of Lanthanides with 1-Phenyl-3-Hydroxytriazene and 1,10-Phenanthroline

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**ABSTRACT:** Lanthanide complexes have garnered significant attention due to their unique properties and wide range of applications in areas such as catalysis, materials science, and medical imaging. This paper aims to elucidate the stabilities of ternary complexes of Lanthanum (III)Neodymium (III)Samarium (III) and Gadolinium (III)with 1-phenyl-3-hydroxytriazene and 1,10-phenanthroline determined by different methods. The stability sequences for systems consisting of metal ,1-phenyl-3- hydroxytriazene and 1,10-phenanthroline having the molar ratio as 1:2:1, and 1:1:2 determined in both the cases were found in close agreement with each other.

### I. INTRODUCTION

Lanthanides, comprising the 15 elements from lanthanum (La) to lutetium (Lu), exhibit unique electronic configurations that lead to distinctive chemical properties. These properties are exploited in various applications, from industrial processes to advanced technologies in healthcare and energy. Understanding the stability of lanthanide complexes is crucial for optimizing their performance in these applications. This paper reviews the current knowledge on the factors affecting the stability of lanthanide complexes, focusing on the interplay between electronic structure, ligand interactions, and environmental influences.

In recent years there has arisen a considerable interest in the study of ternary complexes because of their utility in biological and analytical chemistry. The ternary species are made up of the central metal ion and of ligands of two kinds, in addition to solvent molecules required to make up the coordination sphere. These complexes are considered to have been formed by either of the two ways: (1) when the first ligand do not satisfy all the coordination requirements of a metal ion so that the second ligand reacts with the species and uses all the remaining coordination sites or (1) the first ligand satisfies all the coordination positions of metal ion but does so in a purely dative fashion, so that this complex bears an overall positive charge of the original central metal ion and it associates with a second ligand of suitable anionic charge to form ternary complex. This of course requires the size of metal ion to be large enough so that the second ligand can approach it.

### II. STABILITY OF TERNARY COMPLEXES

When the stabilities of ternary and binary complexes are compared, it is convenient to consider the dimensionless mixing constant  $K_M$  for the formation of a mole of mixed complex. This is the constant sometimes directly measured experimentally and often reported by calculating it from other constants for reactionssuch as.



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$$M + iA + jB \square MA_iB_j$$
$$MA_n + nB \square MB_n + nA$$
$$K_{M(ij)} = \frac{K_{ij}}{K_{no}^{1/n}K_{on}^{1/n}}$$
$$K_{M(ij)} = K(+jB - jA)_{ij} / K(+nB - nA)_{on}^{j/n}$$

Thus a major contribution to K will free statistical arguments alone and the stabilization constant which for ligands of equal density can be given as  $\log K_s = \log K_M - \log(n/i)$ 

Where n/i is the binomial coefficient. The stabilization constant then measures extra stability of the ternary complex due to electrostatic forces, geometric factors, solvent effect, etc. to the statistical factors.

#### **III. EXPERIMENTAL**

All Analar grade or its equivalent chemicals were used for the preparation of the solution. the molar solutions of sodium hydroxide, sodium perchlorate, perchloric acid were prepared and diluted so as to obtain solutions of requisite strength as discussed earlier. The molar solutions of hydroxytriazenes and 1,10-phenanthroline dihydrochloride were also obtained by diluting the stock solutions in dioxane and double distilled water respectively. The metal ion solutions were prepared from their respective metal oxides and the metal contents were estimated by usual standard methods. Irwing -Rossotti pH-titration technique was implemented for the determination of stability constants of ternary complexes

**Calculations**: The formation functions and free 1igand exponent (PA) values have been calculated using the expression for binary systems While evaluating PA values, the pK values of both the ligands were taken Into consideration as the ternary complexes are formed by the simultaneous interactions of metal ions with both ligands

The stepwise stability constants have also been calculated by using pointwise method. The graphical values of n and pA from formation curves have been used to cover the entire range for calculating stability constants.

#### Table 1:Stability constants of mixed-ligand (1:1:2) metal complexes of 1-phenyl-3-hydroxytriazene and 1,10phenanthroline

Metal	$logk_1k_2k_3$	$logk_1k_2k_3$
Lanthanum	37.86	37.84*
Neodymium	41.87	41.86*
Samarium	40.72	40.75*
Gadolinium	40.61	40.59*

## Table2: Stability constants of mixed-ligand (1:2:1) metal complexes of 1-phenyl-3-hydroxytriazene and 1,10-phenanthroline

Metal	$logk_1k_2k_3$	$logk_1k_2k_3$
Lanthanum (III)	37.79	37.76*
Neodymium (III)	41.68	41.72*
Samarium (III)	41.61	41.66
Gadolinium (III)	41.42	41.47*



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## Table3: Stability constants of binary (MA2 and ML) and ternary(MA2L) metal complexes of 1-phenyl-3-hydroxytriazone (A)and 1,10-phenanthroline (L)

Metal	$\log K^M_{MA_2L}$	$\log K^M_{_{MA_2}}$	$\log K_{ML}^{M}$
Lanthanum (III)	37.79	18.91	0.68
Neodymium (III)	41.68	19.55	1.31
Samarium (III)	41.61	19.31	0.37
Gadolinium (III)	41.42	19.56	0.28

## Table 4: Stability constants of binary (MA and ML2) and ternary(MAL2) metal complexes of 1-phenyl-3-hydroxytriazone (A)and 1,10-phenanthroline (L)

Metal	$\log K^M_{MAL_2}$	$\log K_{MA}^M$	$\log K^M_{_{ML_2}}$
Lanthanum (III)	37.86	9.50	0.79
Neodymium (III)	41.87	9.79	2.07
Samarium (III)	40.72	9.69	0.50
Gadolinium (III)	40.61	9.85	0.36

### IV. RESULT AND DISCUSSION

**Stability Sequence**: The ternary complexes of lanthanides have been studied. The stability sequences for systems consisting of metal ,1-phenyl-3-hydroxytriazene and 1,10-phenanthroline having the molar ratio as 1:2:1, and 1:1:2 are given in Tables3 and 4 respectively. The results determined in both the cases were found in close agreement with each other. In both types of complexes, the stability sequence for lighter lanthanides has been found to be similar. In both the cases neodymium seems to form more stable complexes. Neodymium ternary complexes of hydroxytriazenes and 1,10-phenanthroline are most stable among the lighter lanthanide complexes under study. This may possibly be due to high degree of covalency in metal ligand bond

Stability sequence for ternary metal complexes (MA<sub>2</sub>L) of Table 3 1-phenyl-3- hydroxytriazene and 1,10-phenanthroline La<Gd<Sm<Nd

Stability sequence for ternary metal complexes (MAL<sub>2</sub>) of Table 4 1-phenyl-3- hydroxytriazene and 1,10-phenanthroline La<Gd<Sm<Nd

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