

Physicochemical Studies of Binary Complexes of Lanthanides with N, O-Donor Ligands

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Abstract. The stability constants of binary complexes of La(III), Nd(III), Sm(III), Gd(III), Dy(III) and Ho(III) with N, O- donor ligands (hydroxytriazenes) have been determined in 50% (V/V) dioxane-water mixture at constant ionic strength, 0.15M sodium perchlorate, and at $30 \pm 0.5^\circ\text{C}$ using Irving-Rossotti potentiometric titration technique and the constants were evaluated by Bjerrum's half integral method and the results are in close agreement with those evaluated by pointwise method. The lanthanide complexes of hydroxytriazenes have been synthesized with rare earths to ligand ratio 1:4. The elemental analyses and molecular weight determination have shown stoichiometry as 1:4. The IR spectral studies have been made to study the nature of metal-ligand bond. In these complexes, lanthanides have eight coordination number.

1. Introduction

Hydroxytriazenes as analytical reagent and structures and stabilities of their 3d-transition metal complexes are reported in literature¹ but no significant information is available regarding their 4f-transition metal complexes. The present communication deals with the stabilities, preparation and spectroscopic studies of lanthanide complexes of hydroxytriazenes.

2. Experimental

The ligands 1-phenyl-3-hydroxytriazene (PHT), 3-methyl-1-phenyl-3-hydroxytriazene (MPHT) and 1,3-diphenyl-3-hydroxytriazene (DPHT) were prepared by coupling diazonium salt with an appropriate hydroxylamine as described in the literature²⁻⁴.

The perchlorate solutions were prepared by treating calculated amount of metal oxides with perchloric acid of requisite strength. The metal contents were estimated by usual standard methods⁵. Carbonate free sodium hydroxide solution (0.1M) and perchloric acid solution (1.0M) were prepared and standardised. Dioxane was purified by Weissberger's method⁶. Ligand solution (0.02M) and sodium perchloric solution (1.0M) were prepared in dioxane and double distilled water respectively.

The pH-metric titrations of the ligand as such and in presence of metal ions were carried out using E. C. digital pH meter (Model No. 5651) with the combined glass and calomel electrodes system at $30 \pm 0.5^\circ\text{C}$ in an atmosphere of nitrogen at constant ionic 0.1M NaClO_4 in 50% dioxane-water medium. The titrations of perchloric acid as such and in presence of ligand were also carried out under identical conditions. The hydrolysis corrections were made wherever necessary using the titration curves of the mineral acid as such and in presence of the metal ion under identical conditions as cited above.

The values of \bar{n}_A , \bar{n} , \bar{n}_1 and pA have been calculated from the above titration curves using the Irving-Rossotti method⁷. The stability constant data evaluated by Bjerrum half integral method were found in close agreement with those evaluated by pointwise method. The PC/XT computer was used for calculating the stability constants. The results are given in the Table 1.

Preparation of Lanthanide Complexes of DPHT: La(III), Nd(III), Sm(III), Gd(III), Dy(III), and Ho(III) complexes were prepared by refluxing an ethanolic solution of metal perchlorate and DPHT in the ratio 1:4 for nearly two hours at an optimum pH (5-6, adjusted by gradual addition of alcoholic ammonia). The solid complexes were separated, filtered, washed and dried in vacuum.

These complexes were found stable towards light, heat and air. They do not melt but decompose on heating beyond 300°C . The complexes do not dissolve in commonly available solvents but dissolve in glacial acetic acid, DMSO and DMF. The analytical data as found experimentally are in close agreement with the calculated values. The molecular weight of the complexes was determined cryoscopically in glacial acetic acid. These results reveal 1:4 stoichiometry for these complexes.

The infrared absorption spectra of these complexes were obtained in KBr wafer phase using Perkin Elmer Infrared spectrophotometer model 1700.

3. Results and Discussion

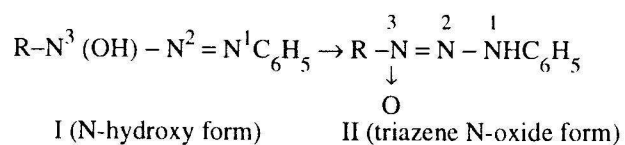
The first stepwise stability constant ($\log k_1$) data (cf. Table I) do not show any linear relationship with the reciprocal of ionic radii or with overall ionisation potential of tripositive lanthanide ions. This suggests that metal-ligand bond is not essentially only ionic. This may possibly be due to ligand structural changes and probable involvement of 4f-orbitals in bond formation. Similar observations have been made by Duncan⁸ in the studies of lanthanide complexes.

The spectroscopic studies⁹ have shown that the hydroxytriazenes exist in tautomeric equilibria.

Table I.

Metal	Log k ₁	Log k ₂	Log k ₃	Log k ₄	Log k
I. 1-phenyl-3-hydroxytriazene					
La(III)	9.50 9.49	9.41 9.40	9.36 9.34	9.22 9.21	37.49 37.44
Nd(III)	9.79 9.78	9.76 9.78	9.72 9.71	9.58 9.59	38.85 38.90
Sm(III)	9.69 9.67	9.62 9.65	9.55 9.55	9.47 9.46	38.33 38.33
Gd(III)	9.85 9.85	9.71 9.75	9.67 9.67	9.59 9.60	38.82 38.87
Dy(III)	10.12 10.22	9.76 9.73	9.72 9.70	9.66 9.65	39.26 39.30
Ho(III)	11.85 -	9.81 9.83	9.77 9.79	9.71 9.69	41.14 -
II. 3-Methyl-1-phenyl-3-hydroxytriazene (MPHT)					
La(III)	9.73 9.70	9.64 9.62	9.59 9.61	9.43 9.42	38.89 38.35
Nd(III)	9.88 9.89	9.79 9.79	9.75 9.74	9.66 9.71	39.08 39.13
Sm(III)	9.92 -	9.79 9.76	9.72 9.70	9.58 9.58	39.01 -
Gd(III)	9.78 9.75	9.59 9.60	9.54 9.52	9.39 9.42	38.30 38.29
Dy(III)	9.92 9.94	9.84 9.85	9.79 9.81	9.69 9.68	39.24 39.28
Ho(III)	11.63 11.63	9.89 9.85	9.85 9.84	9.76 9.75	41.13 40.97
III 1,3-diphenyl-3-hydroxytriazene (DPHT)					
a(III)	9.04 9.03	8.90 8.86	8.68 8.69	8.44 8.43	35.06 35.01
Nd(III)	9.59 9.59	9.50 9.53	9.45 9.49	9.32 9.31	37.86 37.92
Sm(III)	9.48 9.48	9.40 9.41	9.36 9.31	9.24 9.28	37.48 37.48
Gd(III)	9.49 9.44	9.41 9.43	9.36 9.39	9.24 9.25	37.50 37.51
Dy(III)	9.59 9.60	9.40 9.38	9.35 9.36	9.30 9.29	37.64 37.63
Ho(III)	10.99 10.94	9.37 -	9.33 9.33	9.25 9.25	38.94 -

Note : Data in second column in each case evaluated by Point wise method.



Both PHT and DPHT exist predominantly in N-hydroxy form whereas MPHT exists predominantly in triazene N-oxide form. The metal complexes formed by PHT and DPHT involve N-OH acidic functional group whereas metal complexes formed by MPHT involve -NH acidic functional group as shown below :

The stability sequence in lanthanide complexes of PHT and DPHT has been found as, La < Sm Gd < Nd; Dy < Ho, while in case of MPHT, the stability sequence has been observed as, Gd < La < Sm < Nd; Dy < Ho.

This difference in stability sequence of lanthanide complexes of two types of ligands is attributed to the difference in functional groups.

The infrared spectrum of DPHT in KBr wafer phase shows absorption bands at 3160 cm^{-1} due to N-OH stretching vibrations and its deformation mode at 1315 cm^{-1} . These absorption bands disappear in all its lanthanide complexes indicating that N-OH proton has been lost in the complexation reactions. Further the absorption band due to N=N group at 1415 cm^{-1} is displaced to a low frequency region $1410\text{-}1400\text{ cm}^{-1}$ indicating -N=N- as coordinating group in metal complexes. The absorption bands near 450 cm^{-1} and near 630 cm^{-1} in all metal complexes have been assigned to M-O stretching and lattice water vibrations respectively.

The factors such as ligand structural changes, probable participation of f-orbitals in metal-ligand bond formation, the back donation from the central metal ion to vacant orbitals or π^* antibonding orbitals etc. seem to influence the stabilities of lanthanide complexes of hydroxy triazenes.

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