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Some Rare Earth Chelates of N-thioacetyl-N-phenylhydroxylamine

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The stability constants of La(III), Pr(III), Nd(III), Sm(III), Gd(III) and Y(III) with N-thioacetyl-N-phenylhydroxylamine have been determined potentiometrically in 50% dioxane aqueous medium at 0.1 M ionic strength at 30°C. The method of Bjerrum-Calvin has been employed to find the value of formation constants, Block McIntyre and pointwise calculation methods have been applied for the calculation of stepwise and overall stability constants of rare-earth ions. The stability sequence for 1 : 1 (metal : ligand) complexes is found to be:

$$\mathrm{Sm} > \mathrm{Y} > \mathrm{Gd} > \mathrm{Nd} > \mathrm{Pr} > \mathrm{La}$$

INTRODUCTION

Thiohydroxamic acids are known to act as antimicrobial agents[1-3]. The chelating behaviour of thiohydroxamic acids has been investigated and reported from our laboratories[4-9]. Sulphur is one of the most important donor atom being able to form both σ and π bonds. In the present investigations-N-thioacetyl-N-phenyl hydroxylamine has sulphur and oxygen as potential binding sites. Thus they are used for the study of the stability and structure of rare-earth chelates.

EXPERIMENTAL

All the chemicals used were of analaR grade. N-thioacetyl-N-phenyl hydroxylamine was prepared by thionation of N-acetyl-N-phenyl hydroxylamine with phosphorous pentasulfide and recrystallised from alcohol[10]. The purity of ligand was checked by elemental analysis, TLC and IR spectra. Fresh solutions of metal ions were prepared by dissolving an excess of pure metal oxide in perchloric acid to prevent hydrolysis. The solutions were boiled to remove any carbon dioxide present and then diluted to requisite strength. The metal content was estimated by titration with EDTA[11]. The entire study was carried out in an inert atmosphere of nitrogen and fresh solutions were used to avoid the effects of ageing and oxidation.

10 ml of N-thioacetyl-N-phenylhydroxylamine was pipetted into a titration vessel. A sufficient amount of 0.02 M hydrochloric acid was used to lower the pH to about 2. The ionic strength was maintained at 0.1 M by adding 2.5 ml. of 2M KCl solution. When titrating in the presence of metal ion with 0.02 M NaOH, a 5 ml metal solution (0.002 M) was used. The total volume was made upto 50 ml by adding varying amount of

dioxane and air free double distilled water such that the resulting solution constitute a 50%(V/V) dioxane-water mixture to provide suitable solubilities for the measurements. The temperature of the solution was maintained at **Ca.** 30±0.5°C.

RESULTS AND DISCUSSION

Hydroxamic acids and their respective thio analoges are known to act as bidentate ligands in chelation reactions with metal ions[12-14]. Metal ions may either accept π bonding to be mixed with their vacant orbitals or donate π bonding to mix with the vacant orbitals of donor atoms. The π electron density around the donor atom influences the metal-ligand bond. The rare-earth ions exhibit a weaker complexing tendency compared to transition metal ions. This may be due to the larger size of rare-earth ions and the non-availability of orbitals for covalent bond formation. However, the presence of excess of ligand in this study results in suppressing the hydrolysis of rare-earth ions and thus more co-ordination sites would be available for complexation.

Sulphur containing ligands are considered to be soft bases due to the polarisation of sulphur by the metal ion. Sulphur atom has vacant d-orbitals which can be used for $d_\pi - p_\pi$ bonding but such types of bonding is possible only with transition metals having electrons in d_π orbitals. Such possibility has been ruled out in case of rare-earths.

The stepwise and overall formation constants of rare-earth chelates have been evaluated by the method of Bjerrum-Calvin. The stabilities of the complexes as accounted from log K_1 follow the order (Table 1).

$$Sm > Y > Gd > Nd > Pr > La$$

A plausible explanation for this trend is that rare-earth ions differ in the number of 4f-electrons[15], which are effectively shielded from interaction with ligand orbitals by electrons in the 5s and 5p orbitals. Sometimes hybridisation may involve normally unoccupied higher energy orbitals (e.g. 5d, 6s and 6p). This is to be expected in most strongly co-ordinated ligands. Hence rare earths usually form predominantly ionic compounds. However, the possibility of covalent interaction can not be excluded. The mutual repulsion of highly negatively charged ligands hinders the formation of higher mononuclear complexes and a poly-nuclear chain structure is favoured[16]. Y(III) and Gd(III) have zero crystal field stabilization and it would be expected on the basis of size, that Y(III) complex of a given ligand will be more stable than the corresponding Gd(III) complex. A perusal of Table 1 shows that log K_1 value of the Y(III) chelates is quite close to that of to Gd(III) chelate.

1 : 3 complexes are formed with the metal studied. The stability data as calculated using Block and McIntyre and pointwise calculations methods are in reasonable agreement with the Bjerrum-Calvin graphical method as shown in Table 1.

TABLE 1

STABILITY CONSTANTS OF METAL CHELATES OF N-THIOACETYL-N-PHENYLHYDROXYLAMINE

Metal ion	log K_1 $n = 1.5$	log K_2 $n = 1.5$	log K_3 $\bar{n} = 2.5$	log β
La^{+3}	5.85	4.11	2.71	12.67
	5.88	4.08	2.75	12.69*
	5.83	4.13	2.70	12.66†
Pr^{+3}	6.20	4.51	3.16	13.87
	6.22	4.54	3.13	13.89*
	6.20	4.49	3.18	13.87†
Nd^{+3}	6.35	4.61	2.96	13.92
	6.39	4.64	2.99	14.02*
	6.37	4.60	2.94	13.91†
Sm^{+3}	6.90	5.86	4.11	16.87
	6.87	5.85	4.14	16.86*
	6.92	5.84	4.10	16.86†
Gd^{+3}	6.75	5.36	3.51	15.62
	6.77	5.38	3.47	15.62*
	6.74	5.33	3.52	15.59†
Y^{+3}	7.20	5.41	3.61	16.22
	7.18	5.43	3.59	16.20*
	7.19	5.44	3.64	16.27†

*Block and McIntyre method.
†Pointwise calculation method.

The stability data alone could not ascertain the structure of the metal chelates and hence the solid rare-earth chelates of N-thioacetyl-N-phenyl hydroxylamine have also been isolated. The structural aspects of these chelates were investigated by elemental analysis and IR spectroscopy. N-thioacetyl-N-phenylhydroxylamine exhibit intense band at 3350 cm^{-1} due to stretching of the intramolecularly hydrogen bonded-OH group. The absence of this bond in the complexes indicate the deprotonation of —OH group and consequently co-ordination of oxygen atom to the metal. The $\rangle$C=S stretching of the ligand occured at 1075 cm^{-1} and on complexation this band shifted to lower energy by 20–30 cm^{-1} indicating the co-ordination of sulphur to metal atom. Solution as well as solid studies of these complexes indicated the formation of 1 : 3 (metal : ligand) chelates.

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