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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Mathur, S. P. and Bhandari, C. S.(1981) 'Chelating Behavior of Thiohydroxamic Acids. Part I. Electrometric Studies of Lanthanon Chelates', *Journal of Macromolecular Science, Part A*, 15: 4, 609 – 612

To link to this Article: DOI: 10.1080/00222338108056752

URL: <http://dx.doi.org/10.1080/00222338108056752>

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Chelating Behavior of Thiohydroxamic Acids. Part I. Electrometric Studies of Lanthanon Chelates

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ABSTRACT

The logarithms of the successive and overall stability constants of complexes of La(III), Pr(III), Nd(III), Sm(III), Gd(III), and Y(III) with N-thiobenzoylhydroxylamine have been determined potentiometrically in 70% (v/v) dioxane-aqueous medium at 0.1 M ionic strength at $30 \pm 1^\circ\text{C}$. The method of Bjerrum-Calvin has been used to find the values of formation data. Least square, Block and McIntyre, and Schroder methods have been applied for the calculation of stepwise and overall stability constants of lanthanon chelates. The stability sequence for 1:1 (metal:ligand) complexes is found to be $\text{Sm} > \text{Nd} > \text{Gd} > \text{Pr} > \text{La} > \text{Y}$.

INTRODUCTION

This communication forms a part of our continued investigations on the chelating ability of a series of hydroxamic acid analogs [1-6]. Very little work appears to have been carried out on the chelating behavior of thiohydroxamic acids, especially in solutions. The aim of the present investigation is to study the complexing behavior of N-thiobenzoylhydroxylamine with trivalent ions; viz., La^{3+} , Pr^{3+} , Sm^{3+} , Gd^{3+} , and Y^{3+} . The stepwise and overall stability constants of these lanthanon chelates have been determined by the Bjerrum-Calvin pH

titration technique [7]. The study has established the existence of 1:3 (metal:ligand) chelates for Nd^{3+} , Sm^{3+} , and Y^{3+} and 1:2 complexes of La^{3+} , Pr^{3+} , and Gd^{3+} .

EXPERIMENTAL

Materials

N-Benzoylhydroxylamine was prepared by a slightly modified method of Destraz [8], and thionation of N-benzoylhydroxylamine with phosphorous pentasulfide yielded the N-thiobenzoylhydroxylamine [9].

Metal solutions were prepared by treating an excess of pure oxide of metal in perchloric acid. The solutions were boiled to remove any carbon dioxide present in solutions and then were diluted to the requisite strength.

All chemicals used were of Analar grade. A Cambridge bench type pH meter was used for all pH measurements.

Procedure

Ten milliliters of N-thiobenzoylhydroxylamine (0.04 M) in dioxane was pipetted into a titration vessel. A sufficient amount of 0.02 M hydrochloric acid was added to lower the pH to about 2. The ionic strength was maintained at 0.1 M by adding 2.5 mL of 2 M potassium chloride solution. When titrating in presence of metal ions, 5 mL of metal solution (0.002 M) was taken, or the total volume of the content was made to 50 mL by adding varying amounts of dioxane and double distilled water so that the resulting solution became a 70% v/v dioxane-water mixture. The temperature of the solution was maintained at $30 \pm 1^\circ\text{C}$ and an atmosphere of nitrogen was maintained.

RESULTS AND DISCUSSION

Hydroxamic acids are known to act as bidentate ligands and to form chelates with metal ions [10, 11]. N-Thiobenzoylhydroxylamine exists in thione-thiol tautomeric forms in solution, and our investigations have established that the thiol form dominates in chelation.

The rare-earth ions exhibit a weaker complexing tendency compared to transition metal ions. This may be due to 1) the larger size of the rare-earth ions and 2) the nonavailability of 4f orbitals for covalent bond formation. The formation of higher mononuclear complexes is hindered due to the mutual repulsion of highly negatively charged ligands which prefer to form polynuclear chelates. Table 1 summarizes the stepwise and overall stability constants as calculated

TABLE 1. Stepwise Stability Constants of Lanthanone Chelates at $30 \pm 1^\circ\text{C}$

Metal ion	Log K_1	Log K_2	Log K_3	Log β
La^{3+}	6.51	4.52	-	11.03
	6.45	4.50	-	10.95 ^a
	6.49	4.53	-	11.02 ^b
	6.52	4.53	-	11.05 ^c
Pr^{3+}	6.55	4.62	-	11.17
	6.46	4.61	-	11.07 ^a
	6.54	4.64	-	11.18 ^b
	6.57	4.64	-	11.21 ^c
Nd^{3+}	6.70	4.77	3.42	14.89
	6.64	4.79	3.38	14.81 ^c
Sm^{3+}	6.80	5.12	3.62	15.54
	6.73	5.06	3.65	15.44 ^c
Gd^{3+}	6.60	4.72	-	11.32
	6.55	4.67	-	11.22 ^a
	6.54	4.77	-	11.31 ^b
	6.58	4.74	-	11.32 ^c
Y^{3+}	6.31	4.37	3.08	13.76
	6.36	4.30	3.12	13.78 ^c

^aLeast square method.^bSchroder method.^cBlock and McIntyre method.

by different methods. The stability order for log K_1 is found to be $\text{Sm} > \text{Nd} > \text{Gd} > \text{Pr} > \text{La} > \text{Y}$. Log K_1 values of the yttrium(III) chelate is found to be quite close to the value of the lanthanum(III) complex. This is possibly either due to lack of ligand field stabilization, which make it convenient to move yttrium very close to lanthanum(III), or to the nature of the ligand. The unusual behavior of gadolinium(III) is expected due to the "gadolinium break." The hindrance in formation of metal chelates may be attributed to either the poor donating power of the sulfur atom for rare-earth ions or to some steric hindrance caused by the larger size of the sulfur atom.

ACKNOWLEDGMENT

Thanks are due to Prof. J. P. Tandon, Head, Department of Chemistry, University of Rajasthan, Jaipur, India, for providing the necessary facilities.

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Accepted by editor December 4, 1979

Received for publication March 5, 1980