

1953

## Some Aspects of the Chemistry of Samarium (II) Compounds

Alexander I. Popov  
*State University of Iowa*

Wesley W. Wendlandt  
*State University of Iowa*

*Let us know how access to this document benefits you*

Copyright ©1953 Iowa Academy of Science, Inc.

Follow this and additional works at: <https://scholarworks.uni.edu/pias>

---

### Recommended Citation

Popov, Alexander I. and Wendlandt, Wesley W. (1953) "Some Aspects of the Chemistry of Samarium (II) Compounds," *Proceedings of the Iowa Academy of Science*, 60(1), 300-303.

Available at: <https://scholarworks.uni.edu/pias/vol60/iss1/36>

This Research is brought to you for free and open access by the Iowa Academy of Science at UNI ScholarWorks. It has been accepted for inclusion in Proceedings of the Iowa Academy of Science by an authorized editor of UNI ScholarWorks. For more information, please contact [scholarworks@uni.edu](mailto:scholarworks@uni.edu).

## Some Aspects of the Chemistry of Samarium (II) Compounds

By ALEXANDER I. POPOV AND WESLEY W. WENDLANDT

Although the normal oxidation state of the rare earth elements is the tripositive one, several of them are capable of exhibiting either a lower or a higher valence of variable degrees of stability. Of particular interest in this investigation was the divalent state exhibited by samarium.

It is well known that half filled electronic shells tend to be rather stable. Divalent europium with electronic configuration of  $Xe\ 4f^7*$  forms quite stable compounds which are slowly oxidized by water. Another stable rare earth divalent ion is  $Yb^{2+}$  where the 4f shell is complete, ( $Xe\ 4f^{14}$ ), divalent samarium ion, on the other hand, only approaches a half filled shell ( $Xe\ 4f^6$ ) and is consequently extremely susceptible to oxidation.

The first known samarium (II) compound was the chloride prepared by Matignon in 1906 (1). Later investigators prepared the bromide (2) and the iodide (3). All of these compounds were obtained by hydrogen or ammonia reduction of the corresponding trivalent halides at elevated temperatures. The iodide can likewise be prepared by the thermal decomposition of the  $SmI_3$  (3).

Several of the divalent samarium compounds have been prepared by metathetical reactions in aqueous solutions; the sulfate, the chromate and the phosphate by Jantsch and Skalla (3) and the fluoride, the citrate and the carbonate by Clifford and Beachell (4). Of all these compounds only the sulfate could be isolated and analyzed.

Several investigators have reported a green colored samarium (II) compound (4, 5) which was, presumably, either a carbonate or a hydroxide. The unusual color is rather interesting since all other compounds of divalent samarium are red.

### EXPERIMENTAL PART

The starting material was samarium sesquioxide obtained from the "Research Chemicals", Burbank, California. It was stated to be 99% pure. The oxide was dissolved in warm 6N hydrochloric acid and the solution was evaporated to dryness on a steam bath.

\*Xe = Xenon configuration.

The crystals obtained were ground to a fine powder and then dehydrated with thionyl chloride according to the method of Eyring and Machlan (6). Analysis of the product showed that it was completely anhydrous.

An attempt was made to reduce samarium (III) chloride with a solution of sodium in liquid ammonia. A weighed amount of the anhydrous trichloride was placed on a sintered glass disk in an enclosed glass system, and cooled to dry ice temperature after which several milliliters of the sodium solution were introduced over it. After contact of several minutes the solution was filtered and the excess of sodium was removed by repeated washings with liquid ammonia. The product was then allowed to warm up to the room temperature in a nitrogen atmosphere.

The product obtained from the above reduction has the characteristic red-brown color of samarium (II) compounds. It had, however, increased noticeably in volume due to the formation of unstable ammonia complexes. In the air the sample freely gave off ammonia, and rapidly changed its color to white, indicating that it was reoxidized to the trivalent form. In view of the difficulty involved in obtaining a definite sample, no quantitative analysis on the product was attempted.

Samarium (II) chloride used in further investigations was obtained by hydrogen reduction of the trichloride at 650° for three hours. It was found that only very pure hydrogen could be used, since the presence of traces of oxygen would result in the formation of the oxychloride. "Deoxo" cylinders (Baker & Co., Newark, N. J.) were found to be quite satisfactory in removing oxygen and the moisture was retained by a liquid nitrogen trap.

The reduction products were analyzed volumetrically by placing them in an excess of potassium dichromate-potassium sulfate solution and back titrating with ferrous ammonium sulfate (7). The yields were mostly between 84% and 86% although on several occasions, they were as high as 95%.

Contrary to the literature reports (1) it was found that samarium (II) chloride was quite stable in dry air. A sample was kept open to air for as long as one month without undergoing any appreciable change in composition.

Several new compounds of divalent samarium were prepared by metathetical reactions. About 100 mgs. sample of  $\text{SmCl}_2$  was dissolved in 5 ml. of ice cold water and the solution was immediately poured into a 15 ml. centrifuge tube containing 5 ml. of ice cold solution of the sodium or potassium salt of the desired anion.

Immediately after mixing the solution was centrifuged and the precipitate of the corresponding samarium (II) compound was found collected on the bottom of the tube. In this manner the sulfite, the borate, the pyrophosphate and the phosphite were prepared.

In all cases the precipitate decomposed very rapidly when taken out of water. If left in water, it lasted up to several hours. The sulfite and the borate were in the form of red-orange crystals, while the pyrophosphate and the phosphite were red-brown.

When samarium (II) chloride is added to a concentrated solution of sodium carbonate, immediately a red-brown precipitate of  $\text{SmCO}_3$  is obtained. However, on standing for approximately 15 minutes, the precipitate changes to bright green and then slowly oxidizes to colorless trivalent form.

Addition of samarium (II) chloride to a solution of sodium hydroxide likewise produced a green precipitate. The color is considerably more pale than that of the precipitate obtained from the carbonate solution, however, as this difference may be due to the state of division of the precipitate, it seems logical to conclude that the green compound is the hydroxide.

Attempts were made to precipitate the green compound in alcoholic solutions of potassium or sodium hydroxides, as mentioned by Clifford and Beachell (4), however, their experiment could not be repeated.

Since organic coordinating compounds have been frequently used to stabilize labile oxidation states of metal ions in solutions, it was thought that perhaps a suitable complexing agent could be found that could stabilize divalent samarium. Over fifty organic complexing agents were tried, partial list of which is given below. The experimental procedure consisted in dissolving about 50 mg. of samarium (II) chloride in 5 ml. of water and then adding this solution to the one containing the complexing agent. The relative stability of the complex was judged by the rate of the disappearance of the red color of the solution. In pure water, from which all dissolved oxygen was previously removed by passing through it a current of hydrogen, the color persisted for approximately two minutes. With practically all of the complexing agents, the color persisted for approximately 2-3 minutes. A notable exception was the antipyrine (1-phenyl-2,3-dimethyl pyrolozone-5) solution where color persisted for as long as 20 minutes.

Possible use of a number of organic solvents in the stabilization of samarium (II) complexes was investigated. The results were

negative since samarium (II) chloride proved to be insoluble in all the solvents tried.

**Table 1**

Organic Complexing agents used in this investigation.

1. Anti pyrine	8. Hydrazine hydrate
2. Ammonium nitrosophenylhydroxylamine	9. Ethylene diamine
3. Ethylene dinitrilo tetraacetic acid	10. 1,10 phenanthroline
4. Acetyl acetone	11. Phenyl hydrazine hydrochloride
5. 3-methyl-5-pyrozalone	12. Ethyl amine
6. dipyridyl	13. Acetonyl acetone
7. Imidazole	14. Methyl amine
	15. P-phenylene diamine

**Literature Cited**

1. C. Matignon, *Compt. Rend.*, 142, 83 (1906); *Ann. de chim.*, 8 VIII, 402, (1906).
2. Prandtl, W. and H. Kogel, *Z anorg. allgem. chem.* 172, 265 (1928).
3. Jantsch, G. and N. Skalla, *Z anorg. allgem. Chem.* 193, 391 (1930).
4. Clifford, A. F. and H. C. Beachell, *J. Am. Chem. Soc.*, 70, 2730 (1948).
5. Halleck, L., *Atti. x° congr. intern. chim.*, 2, 671 (1938).
6. Eyring, L. & G. Machlan, to be published.
7. Popov, A. I. and W. Wendlandt, to be published.

DEPARTMENT OF CHEMISTRY  
STATE UNIVERSITY OF IOWA  
IOWA CITY, IOWA