233. *The Absorption Spectrum of Bivalent Samarium.*

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ALL the rare earths have a characteristic valency of three, and the absorption spectra of compounds in which they are tervalent have been studied in great detail. Three of the rare earths, samarium, europium, and ytterbium, can also be bivalent, and the absorption spectrum of europous chloride solution in the visible region (McCoy, *J. Amer. Chem. Soc.*, 1936, **58**, 1577), and the reflection spectrum of ytterbous iodide (Ephraim, Jantsch, and Zapata, *Helv. Chim. Acta*, 1933, **16**, 261) have been investigated. In the case of bivalent samarium, however, nothing is known except the statement that " the reflection spectrum of solid samarium dibromide apparently consists of a diffuse band throughout the visible bearing no resemblance whatever to the discrete bands characteristic of most trivalent rare earth salts " (Selwood, *J. Amer. Chem. Soc.*, 1934, **56**, 2393).

The atomic numbers of samarium and europium being 62 and 63, respectively, the ions Sm^{++} and Eu^{+++} both have 60 electrons; their electronic configurations should therefore be the same, and the ions should show a close similarity in properties depending on this configuration. One of these properties is the magnetic susceptibility, and it is known that the susceptibilities of the two ions in their compounds are almost equal (Selwood, *loc. cit.*; Klemm and Rockstroh, *Z. anorg. Chem.*, 1928, **176**, 181). Another such property is the absorption spectrum, and the object of this work was to investigate that of aqueous samarous chloride, and to see whether it showed any resemblance to that of compounds of tervalent europium. The data available on the absorption spectrum of europium compounds in the ultra-violet are not very concordant with regard to the relative intensities of the bands, and it was therefore decided to study the chloride solution to determine which of the bands are the most intense.

EXPERIMENTAL.

The samarous chloride was prepared by a method similar to that described by Matignon and Cazes (*Compt. rend.*, 1906, **142**, 83). A Pyrex boat containing hydrated samaric chloride was placed in a silica combustion tube surrounded by a tube furnace. A stream of dry hydrogen chloride at about 5 cm. of mercury pressure was passed through the tube, which was heated to 100°. After several hours, when nearly the whole of the water had been driven off, the temperature was slowly raised to 500°. The anhydrous chloride was transferred to an iron boat, in which it was fused in the current of gas at 800°. The hydrogen chloride was now replaced by hydrogen at atmospheric pressure, to reduce the tri- to di-chloride. Before entering the apparatus, the hydrogen (from a cylinder) was freed from all traces of moisture, oxygen, etc., by passage through a tube containing a small quantity of molten sodium heated to 120°. Any ferrous chloride formed owing to attack on the iron boat by the hydrogen chloride sublimed off at the high temperature, and did not contaminate the samarous chloride. After 12 hours, the tube was allowed to cool, and transferred to a Richards sampling box, in which the samarous chloride was removed and ground in an atmosphere of dry carbon dioxide,

FIG. 1.

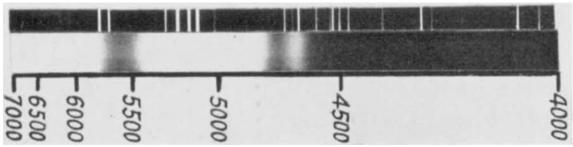

FIG. 2.

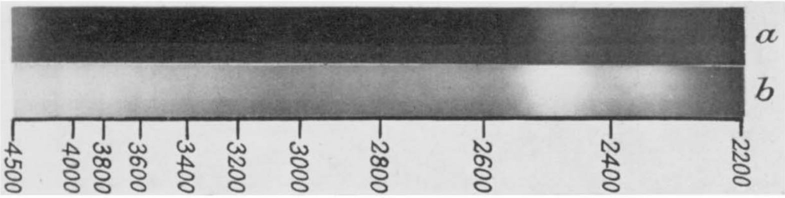

FIG. 3.

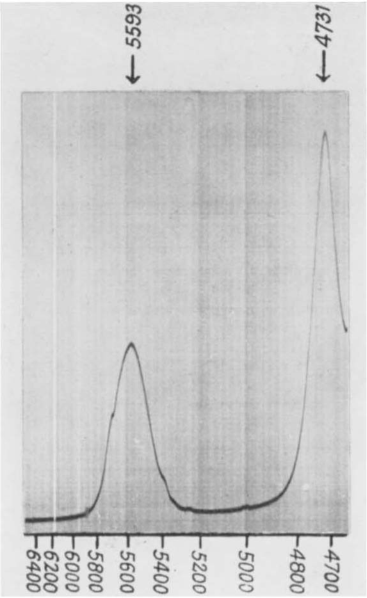

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FIG. 4*a*.

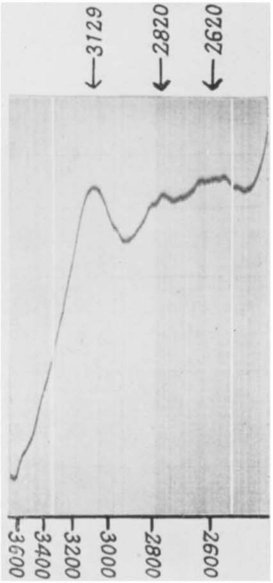


FIG. 4*b*.

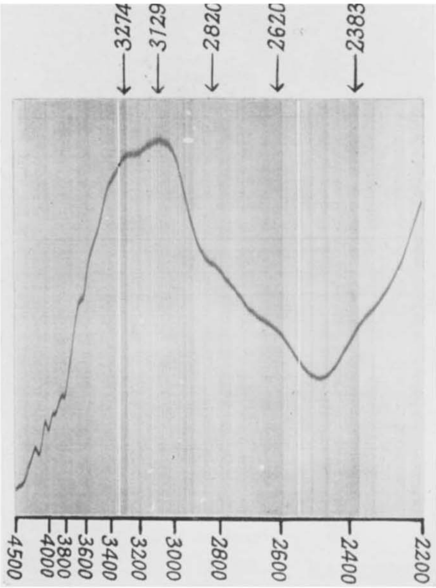


FIG. 4*c*.

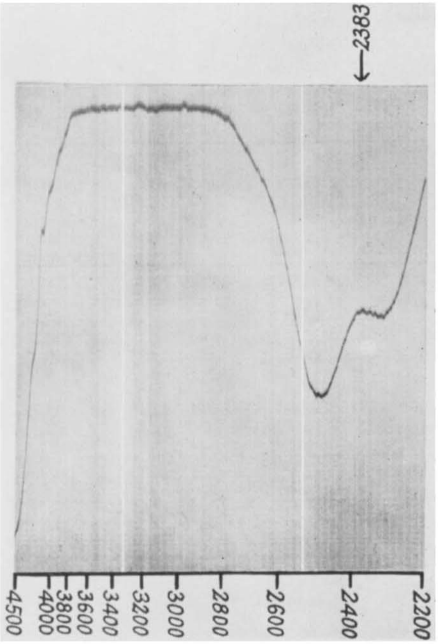
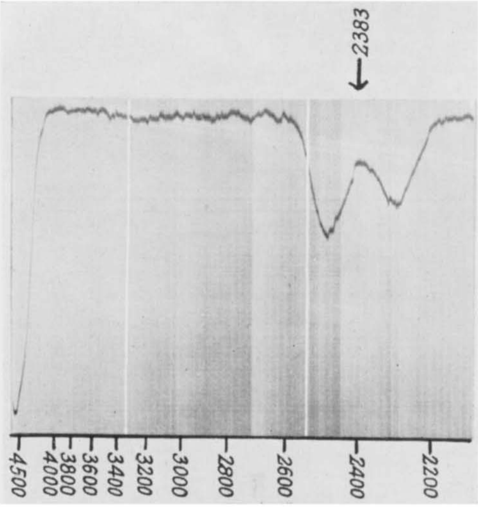


FIG. 4*d*.



being stored in a stoppered specimen tube. This substance could not be ground in the air owing to its rapid decomposition by oxygen or moisture.

Absorption Spectrum.—Samarous chloride is readily soluble in water, giving an intensely red solution. The colour rapidly fades owing to the decomposition $3SmCl_2 + 3H_2O \longrightarrow 2SmCl_3 + Sm(OH)_3 + 3H$, which is usually complete in 2—3 minutes. A quantity of samarous chloride, usually about 50 mg., was placed in a small silica centrifuge tube, 8 mm. in internal diameter and 7 cm. long. This was filled with ice-cold air-free water, and as rapidly as possible stoppered, shaken, and centrifuged to remove any turbidity produced by samaric hydroxide, and placed in front of the spectrograph slit, where it acted as an absorption cell.

For the visible spectrum the light source was a Pointolite lamp, and for the ultra-violet, a hydrogen discharge tube. Calibration was carried out in both cases with a copper arc. In all cases the spectrum of the solution was also recorded after complete decomposition had taken place. In no case was sufficient samarium trichloride produced to show its absorption spectrum. Hence it was not necessary to make any allowance for the trichloride present when spectra were taken with a partially decomposed solution of the dichloride. Photometer records of the spectra were taken with a Zeiss microphotometer in order to determine the positions of the absorption maxima.

For the absorption spectrum of europium trichloride, 10 mg. of Hilger's "H.S." europium oxide were dissolved in 1 c.c. of dilute hydrochloric acid, and the solution placed in a quartz-windowed absorption cell of 0·5 cm. internal thickness. Under these conditions only the more important absorption bands are visible in the photographs. These are listed in the table, the wave-lengths being those given by Prandtl and Scheiner (*Z. anorg. Chem.*, **1934**, **220**, 112).

Results.—Fig. 1 shows the absorption spectrum of samarous chloride in the visible region. There are two well-defined bands with maxima at 5593 and 4731 A., and a region of continuous absorption beginning about 4500 A. and extending into the ultra-violet. Fig. 3 shows the photometer record.

Fig. 2 shows the ultra-violet region; the spectrum *a*, taken with a concentrated solution, shows the region of continuous absorption, which began in the visible, extending to about 2600 A. There is also a band with maximum at 2383 A., and absorption of the extreme ultra-violet. Spectrum *b*, taken with a dilute solution, shows that the region of continuous absorption really consists of a number of overlapping broad bands.

Figs. 4 *a*, *b*, *c*, and *d* are the photometer records of spectra taken with solutions of increasing concentration; 4*a* shows the maximum at 3129 A. and two others at 2820 ± 50 and 2620 ± 50 A., the exact positions of which are difficult to determine; 4*b* shows the maximum at 3129 A. and irregularities in the curve due to maxima at 2820 and 2620, and also at 3274 and 2383 A.; 4*c* and 4*d* show the last maximum clearly, and the extension of the absorption region to 4300 A. suggests the existence of another band of longer wave-length than that at 3274 A.

The results obtained (in all cases the mean values from several photometer records of different plates) are given in the table. It will be seen that there is considerable resemblance between the spectra of bivalent samarium and tervalent europium. Owing to the greater nuclear charge in Eu^{+++} one would expect to find that its wave-lengths are slightly shorter than those for Sm^{++}, and this appears to be the case. However, although the bands of europium are extremely narrow, those of bivalent samarium are among the broadest shown by any rare-earth compound.

Absorption maxima, A.

Sm^{++}	5593		4731		(? *ca.* 4000)	3274	3129	2820 ± 50		2620 ± 50	2383
Eu^{+++}	5255	4656	4651	4647	3943	3179	2980	2867	2853	2513	—

SUMMARY.

The absorption spectrum of samarous chloride solution has been studied, and the positions of the main bands measured. It shows considerable similarity to that of europic chloride, as was to be expected theoretically.

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