THE CHEMISTRY OF EUROPIUM

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Although discovered over forty years ago, the chemistry of europium developed very slowly. Europium is one of the rarest members of the rare earth group. Prior to ten years ago, europium material could be obtained only after long continued fractionation of a large quantity of rare earth compounds. Yntema[1] in 1930 discovered a method whereby europium could be separated rapidly from rare earth mixtures. This discovery not only enabled the rare earth chemist to separate europium quite easily from the rare earths but provided a means whereby sufficient material could be accumulated for extensive research.

Europium is capable of existing in two valence states, the trivalent and the divalent. Trivalent europium exhibits properties which are similar to those displayed by other trivalent rare earths. In addition to these properties trivalent europium may be easily reduced to the divalent state by such reducing agents as aluminum, zinc, or iron. Europium is more easily reduced than any other reducible rare earth.

Divalent europium was discovered by Urbain and Bourion[2] in 1911. They were endeavoring to prepare anhydrous europic chloride by the metathetical reaction between sulfur monochloride and europium oxide. The compound obtained possessed a smaller europium content than that required by the formula $EuCl_3$. This fact led them to investigate the reduction of anhydrous europic chloride by means of hydrogen.

No further work was reported on europous compounds until 1929 when Jantsch and co-workers[3] prepared europous chloride by the reduction of the hydrated europic chloride in an atmosphere of hydrogen chloride and hydrogen. They prepared the sulfate by treating a solution of the dichloride with sodium sulfate. They commend on the insoluble nature of the sulfate. This characteristic together with the stability of the di-iodide led them to postulate the similarity between the divalent rare earth ions and the alkaline earth ions.

Yntema[1] conceived the idea of using these facts in separating europium from other rare earths. He prepared the slightly soluble europous sulfate by electrolyzing a solution of the rare earth chlorides in the presence of dilute sulfuric acid. Practically pure europium was obtained by a single electrolysis. Complete removal however could not be effected. Selwood[4] suggested that divalent europium should possess an ionic radius approximating that of the barium ion and consequently practically quantitative removal could be obtained by a single electrolysis if europous sulfate was coprecipitated with barium sulfate. Brukl[5] found that strontium sulfate was the more efficient co-precipitating agent since the strontium ion and europous ion were practically equal in ionic radii.

McCoy[6] found that an efficient separation could be effected by means of the Jones reductor using amalgamated zinc as the reducing agent. In our laboratory we have studied the optimum conditions for the removal of europium together with some of the properties of europous europium.

The properties of the europous ion are quite different from those of the europic ion. Very dilute solutions of europous ions are colorless. At a concentration of 10mg. per ml. or greater the solutions possess a greenish-yellow color similar to that of chlorine water. Europic solutions are practically colorless. Solid europic compounds possess a faint rose color whereas the europous compounds are generally white. Solutions of europous ions are powerful reducing agents. The reduction potential of the europous-europic ion is approximately 0.4 volts. It is thus one of the highest reducing potentials recorded for an ionic change involving the transfer of one electron. Europous ion is slowly oxidized by dissolved oxygen. If oxygen is absent the europous ion reacts slowly with the water. Hydrogen is discharged and basic salts are precipitated. Similarly to other reducing agents the europous ion is more stable in acid solution than it is in neutral solution. Moderate or strong oxidizing agents oxidize europous ion rapidly to the europic state. Iodine may be used to determine the europous europium content of a solution. Europous europium is capable of reducing ionic silver, copper, mercury, and lead to the metallic state. Ferric iron is reduced to the ferrous state. Sulfite ion is reduced to hyposulfite. Concentrated hydrochloric acid precipitates europous chloride containing two molecules of water from europous solutions. This enables one to obtain very pure europium material. If a sulfate is added to europous solutions, an insoluble precipitate of europous sulfate is obtained. This precipitate is very stable, resisting to a high degree the effect of strong oxidizing agents. Nitric acid however decomposes it rapidly. The sulfate is precipitated in two crystalline modifications depending upon the conditions. The sulfate appears to be the least soluble of the europous compounds. Digestion with sodium carbonate converts the sulfate into the carbonate.

A consideration of the atomic structure of europium enables one to understand more clearly the chemical and physical properties of this element as well as the relationship between it and its neighbors in the rare earth group. In general the addition of an electron takes place in either the outer or next to the outer shell. When we come to the rare earths we find that the electrons are added successively not to the outer shells but to deeper ones. Thus we find that when we come to europium, possessing an atomic number of 63, there are the same number of electrons in the two outermost orbits as there are in the other rare earths but that the 4_4 level has built up to six electrons. These additional electrons are thus shielded from activity and explain why europium possesses certain properties which are characteristic of the rare earths. The electrons in the 4_4 level however would be expected to exert some influence on the properties of the rare earths. After a certain number of electrons have been added to this level, they exert a stabilizing effect enabling one to obtain divalent ions under certain conditions.

Divalent europium possesses 61 electrons in its outer orbits. Trivalent gadolinium and tetravalent terbium also possess 61 electrons. We would thus expect certain properties of these elements in the valences mentioned to be similar and this is found to be the case. Magnetic and optical properties have been shown to be similar.[7] Trivalent europium possesses 60 electrons. Divalent samarium likewise possesses 60 electrons. Consequently we can postulate a similarity between trivalent europium and divalent samarium.

Numerous experiments are still being conducted in order to extend our knowledge of the chemistry of europium. No doubt this information will prove to be not only interesting but also illuminating with respect to the chemistry of the entire rare earth group.

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[1] Yntema, L. F., J. Am. Chem. Soc. *52* 2782 (1930).

[2] Urbain, G., and Bourion, F., Compt. rend. *153* 1155 (1911).

[3] Jantsch, G., Aber, H., and Grubitsch, H., Monatsch. *53-54* 305 (1929).

[4] Selwood, P. W., J. Am. Chem. Soc. *57* 1145 (1935).

[5] Brukl, Angew. Chem. *49* 159 (1936).

[6] McCoy, H., J. Am. Chem. Soc. *57* 1756 (1935).

[7] Pearce, D. W., and Selwood., J. Chem. Ed., *13*, 224 (1936).