

TABLE IV
 POLYMERIC SALTS FROM γ -BROMOPROPYLALKYLAMINES

R =	Amine salt, g.	B. p., Bromoamine, °C. Mm.		Yield, amine, g.	M. p. of polymers, °C.	Formula	Analyses, Br %		
							Calcd. total	Total	Found Ionic
CH ₃	10	29-30	4	2.5	205-210 dec.	(C ₄ H ₁₀ NBr) _n	52.63	52.56	51.89-52.10
C ₂ H ₅	10	31-32	2	7.0	195-199	(C ₅ H ₁₂ NBr) _n	48.19	47.00	46.04
<i>n</i> -C ₃ H ₇	8	37-38	3	1	(C ₆ H ₁₄ NBr) _n	44.44	43.31	41.74
<i>n</i> -C ₄ H ₉	5.2	3.6	100-120	(C ₆ H ₁₆ NBr) _n	41.23	41.33	39.16
<i>i</i> -C ₄ H ₉	6.4	4.4	(C ₇ H ₁₆ NBr) _n	41.23	41.30	35.23

precipitated with dry ether, the total bromine remained approximately constant at 51.96%, but the bromide ion fell to 43.38%. Further attempts to purify the mixture did not lead to any definite product.

A sample of the free polymeric tertiary amine was prepared from the polymeric salt obtained from γ -bromopropylmethylamine. The salt used in this experiment contained 50.3% bromine, and 49.07% bromide ion. A solution of 5 g. of this salt in water was treated with an excess of silver oxide, and then the solution was filtered. The filtrate was again treated with silver oxide to ensure complete removal of bromide ion. The mixture was centrifuged and the liquid filtered. The water was then removed under reduced pressure at room temperature (about 25°). The residue was an amber-colored, viscous, sticky, hygroscopic solid. This material still contained bromine which would react slowly with alcoholic silver nitrate. The water solution of the free polymer was tested with thymolphthalein, and showed a pH of about

9.3. This is slightly less basic than an aqueous solution of trimethylamine, showing that the polymer did not carry quaternary ammonium hydroxide groups. The polymeric amine could not be purified by reprecipitation, and the analysis was not especially significant.

Anal. Calcd. for (C₄H₁₀N)_x: N, 19.44. Found: N, 15.98.

Summary

γ -Bromopropylalkylamines in concentrated solution react intermolecularly to produce polymeric tertiary amine salts. The molecular weight of the linear polymeric salt is dependent on the alkyl group attached to the nitrogen atom, being about 10,000-15,200 when R is methyl, and falling to about 1350-1550 when R is isobutyl.

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The Extraction of Europium from Monazite Residues and the Preparation of Pure Europium Compounds

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The method of separation of europium from other rare earths by reduction with zinc and precipitation as europous sulfate has been described in a preliminary note.¹ An account of further studies of some of the properties of europous salts is given in a later paper.²

The extraction of europium has now been carried out on a larger scale so that a more detailed description of the process of refinement can be given. In the earliest experiments, the starting material had been subjected to long-continued fractional crystallization as double magnesium nitrates in the presence of bismuth nitrate. It contained little besides samarium, europium and gadolinium. For this material, reduction in a Jones reductor two or three times repeated sufficed to give a pure product.¹

When, later, material less rich in europium was used, it was found that modification of the process gave better recoveries of the desired element. Instead of running the rare earth solution through a reductor, it was found more expedient with low grade material to add zinc dust to the solution along with magnesium sulfate. It was also found that the addition of barium chloride as suggested by Selwood³ for use in the electrolytic separation of europium was helpful in giving increased yields. The subsequent purification of the enriched europium concentrates so obtained was carried out in a large reductor as will be described later.

After europium had been extracted successfully from 12 to 15 lots of material varying in amounts from 20 g. to several kilograms and of varying degrees of richness, the separation of the europium

(1) McCoy, *THIS JOURNAL*, **57**, 1756 (1935).

(2) McCoy, *ibid.*, **58**, 1577 (1936).

(3) Selwood, *ibid.*, **57**, 1145 (1935).

content of 386 kg. of rare earth oxalate was undertaken. This material was accumulated during several years as the residue from the technical production of La, Ce, Pr and Nd from Monazite sand from Travancore, India. The large scale operations were carried out in the works of the Lindsay Light and Chemical Co., Chicago.⁴

As the rare earths had been precipitated once as double sodium sulfates, the material doubtless contained but little ytterbium and lutecium, the compounds of which are easily soluble in a solution of sodium sulfate. The material had been freed from all but traces of cerium and thorium. Lanthanum, praseodymium and neodymium had been separated by systematic fractional crystallization of the double magnesium nitrates. The final mother liquors were precipitated with oxalic acid.

The material consisted essentially of the oxalates of Nd, Sa, Eu, Gd, Tb, Dy, Ho, Y and Er, in which the salts of Sa and Gd predominated. The europium oxalate content amounted to about 0.5%. Small amounts of thorium and lead were also present. The material was in the form of a light buff powder.

The 386 kg. of oxalates were boiled in an iron tank, fitted with a stirrer, with 210 kg. of caustic potash and about 1500 liters of water for about an hour, and filtered and washed in an iron suction filter. The hydroxides which resulted were dissolved in hydrochloric acid in a wooden tank to give 1070 liters of chloride solution of density 1.20. The solution settled clear, leaving but a very small residue which was discarded. It was but slightly acid to congo paper.

The chloride solution was reduced in 140-liter portions in a 210-liter stoneware jar, fitted with a cover and stirred vigorously by a 0.25 h. p. motor with stainless steel shaft and propeller.

In making a reduction there was added to the 140 liters of solution, 4 kg. of magnesium sulfate, 0.5 liter of glacial acetic acid and 0.65 kg. of zinc dust. The reduction began at once as was shown by the bleaching of litmus paper. To minimize reoxidation by air, the latter was displaced by a stream of carbon dioxide run into the jar. During the reduction, which required about five hours, a solution of 1 kg. of barium chloride in 20 liters of water was run in slowly. The reaction was judged to be finished when litmus was no longer bleached. The stirring was then stopped and the solution allowed to settle. The residue consisted largely of excess zinc, barium sulfate and europium sulfate, together with considerable rare earths. Usually the solution did not settle clear and had to be filtered. In such case the filter cake was returned to the

jar. The reduction and filtration required the working time of one day.

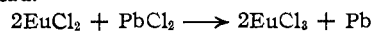
To the whole of the residue left in the jar was added 140 liters of fresh rare-earth chloride solution, together with magnesium sulfate, acetic acid and zinc dust in amounts the same as for the first reduction and the process continuously repeated until, after eight runs, the whole of the solution had been worked up.

The accumulated residue was finally filtered and washed. It was a dark colored mass of high density. The wet cake weighed about 30 kg. It was returned to the jar in which it had been made, and covered with 170 liters of water, 1 kg. of sodium chlorate dissolved in a little water was added, followed by 15 liters of concentrated hydrochloric acid. A vigorous reaction took place as the remaining zinc dust dissolved. At the same time part of the europous sulfate was oxidized and passed into solution. The residue was now pure white. The solution settled clear overnight. The clear solution was drawn off and the rare earths precipitated by adding oxalic acid.⁵

The barium sulfate residue still contained much europous sulfate which was extracted by repeated treatments with hydrochloric acid and sodium chlorate in hot dilute solution. For 140 liters of water 14 liters of concentrated hydrochloric acid and 0.5 kg. of sodium chlorate were used. Each solution after it had settled was drawn off and treated with oxalic acid. A total of five extractions was made and 9 kg. of oxalic acid was used, giving 16 kg. of moist white oxalates.⁶

The oxalates so obtained were converted into hydroxides in a 175-liter glass-lined steam-jacketed kettle where they were boiled with 10 kg. of potassium hydroxide. The washed hydroxides after being dried weighed 7.2 kg. In all the large scale operations only technical grades of chemicals and ordinary water were used.

The dry hydroxides were now shipped to the laboratory for further treatment. They were still quite impure. An analysis² showed about 20% of the whole to be europium hydroxide. The remainder consisted of the same rare earths and other impurities as were contained in the original oxalates. The 7.2 kg. of hydroxides was dissolved in 7.5 liters of concentrated c. p. hydrochloric acid, diluted with water. The solution had a density of 1.27. It was filtered from a small residue. The chloride solution contained a small percentage of lead, which had to be removed in order to avoid trouble in the next operation. This was done by stirring with about 100 g. of amalgamated zinc. The europous salt first formed reacts with the lead chloride to give a black colloidal solution of metallic lead.



The latter coagulates slowly, but after two days it could be filtered clear by the aid of filter-cel. The filtered solution contained but a trace of lead.

The solution was now ready for reduction. The reductor consisted of a 1-liter percolator holding 3.5 kg. of

(5) Zinc can be precipitated as oxalate, but if the solution contains sufficient acid it does not come down nearly as readily as do rare-earth oxalates. By filtering promptly a separation may be made.

(6) The difficulty in extracting the europium is due to the fact that europic sulfate is the least soluble of the rare-earth sulfates [Jackson and Reinacker, *J. Chem. Soc.*, 1687 (1930)] and is much less soluble hot than cold. Hot water was used to facilitate oxidation.

(4) In this plant work I enjoyed the helpful and efficient cooperation of Mr. Mark W. Eichelberger, secretary and superintendent of the Company, to whom I wish to express my warmest thanks. Mr. Sterling Nails also assisted materially.

amalgamated, c. P., 10-mesh zinc. The receiving vessel was a 4-liter wide-mouthed bottle. Into it was put a liter of a hot solution containing 400 g. of magnesium sulfate and 50 ml. of 6 *N* sulfuric acid. The exit tube of the reductor (with rubber tubing connector and screw clamp) reached nearly to the bottom of the receiving bottle. The bottle was closed with a cardboard cap having a hole for the tube. In this case no carbon dioxide or barium chloride was used.

It was found that a hot acidulated magnesium sulfate solution gave rise to the β -form of europous sulfate,² rather than the α -form. This is desirable as the former is less soluble and much denser than the latter. Two receiving bottles were used alternately.

The charge in a receiver was sufficient for 1.5 liters of rare earth solution of density 1.27. A precipitate of europous sulfate forms as the first drop of reduced solution enters the bottle. The rate of flow of solution is such that 1.5 liters are reduced in about forty minutes. The solution settles clear in about an hour longer. The precipitated europous sulfate is very dense and occupies but a small volume. While the first run is settling another 1.5-liter lot of chloride solution is run through the reductor into the alternate receiver charged with magnesium sulfate solution and sulfuric acid as before. The process was thus continued until the whole solution was converted into europous sulfate.

The accumulated filtrates from the process were saved to be again reworked for the small amount of europium they contained. The reduction of the europium by zinc is probably complete, $2\text{EuCl}_2 + \text{Zn} \rightarrow 2\text{EuCl}_3 + \text{ZnCl}_2$, but apparently a small amount (about 1%) is reoxidized before it reacts to form sulfate. The amount is so small that it scarcely pays to try to prevent the re-oxidation.

The europous sulfate is filtered and the cream of wet sulfate poured into a boiling solution of sodium carbonate and sodium hydroxide. The amount of europous sulfate resulting from one run of 1.5 liters of rare earth solution—about 200 g. of moist filter cake—requires 80 g. of sodium carbonate, 15 g. of sodium hydroxide and 1.5 liters of water. It quickly turns light greenish-yellow when boiled due to change into europous carbonate. After ten minutes of boiling it is washed three times by decantation, filtered and washed free of sulfate with hot water. The carbonate is granular and very dense.

When it is dissolved in hydrochloric acid, a light yellow solution of the europous chloride is formed. Considerable other rare earths, as well as thorium, aluminum and perhaps other weak bases are present. If lead is present the

solution will be dark and cloudy. Its purity may be 65 to 70%. It is now oxidized at the boiling point by 8 or 10 ml. of 6 *N* nitric acid.⁷

The nearly colorless oxidized solution is next freed from weak bases by neutralizing it (to congo paper) with basic magnesium carbonate, adding 10 g. of magnesium acetate, and boiling it for a few minutes. The rather heavy precipitate (42 g. wet, in one case) containing but a trace of europium is filtered out. To remove remaining rare earths, the crude europium trichloride is again run through the reductor, precipitated as europous sulfate with 160 g. of magnesium sulfate and 8 g. of sulfuric acid, the sulfate converted into carbonate, the latter dissolved in hydrochloric acid, and the whole process repeated several times. Re-oxidation of the europous chloride solution with nitric acid before running it through the reductor is unnecessary.

After the eighth precipitation as europium sulfate no further rare earths were recoverable from the filtrate, and the solution of europium trichloride resulting showed no absorption bands of other earths. It was again reduced and precipitated as sulfate. This was washed finally with methyl alcohol. The yield was 88 g. of dry europous sulfate. Upon analysis, a portion dried in the oven at 100° and titrated with 0.04 *N* permanganate² showed a purity of 99.7%.

Another lot, made from 1.5 liters of chloride solution of 20% purity, was treated similarly excepting but six precipitations as sulfate were made. The product, 104 g., titrated with standard permanganate, showed a purity of 96.6%. About a week's time is sufficient to prepare approximately 100 g. of pure europous sulfate from the 1.5 liters of chloride solution resulting from 0.5 kg. of crude hydroxide of 20% purity.

Summary

1. A process is described for the extraction of europium from rare earth residues from monazite by reduction of this element to the bivalent state with zinc and subsequent separation as insoluble europous sulfate.

2. Pure europium compounds have been prepared by several repetitions of these reactions.

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(7) If the solution is sufficiently acid no oxides of nitrogen are formed. It is probable that the reaction $10\text{Eu}^{++} + 10\text{H}^+ + 2\text{HNO}_3 \rightarrow 10\text{Eu}^{+++} + \text{N}_2 + 6\text{H}_2\text{O}$ occurs.