

## The Salts of Europium

BY HERBERT N. MCCOY

Although nearly forty years have passed since Demarçay<sup>1</sup> characterized europium as a distinct element, its compounds have been studied little. The only systematic study was that made by Sarkar,<sup>2</sup> who made and analyzed a dozen europic salts. Earlier workers<sup>3-7</sup> had made eight or ten other compounds but many of these had not been analyzed. Europous chloride and sulfate have been made and studied by several workers.<sup>8-12</sup>

With the more abundant supply of europium made available through newer methods<sup>11</sup> of separation and purification, it was deemed worth while to make further studies of the salts of this element. The analytical results are shown in Table I.

In a few cases the results of this study were at variance with earlier work. *m*-Nitrobenzenesulfonate, made by James and Robinson,<sup>6</sup> is said to have 3H<sub>2</sub>O; the analysis of my crystalline product, seemingly pure, indicates 6H<sub>2</sub>O. Europium citrate was made and analyzed by Sarkar,<sup>2</sup> whose figures indicate five molecules of water. My analyses lead to but four. That there are other salts of citric acid is indicated by the fact that only by following a definite procedure could this substance be obtained pure. When 4.0 g. of europium acetate in 30 cc. of cold water was mixed with 6.3 g. of citric acid in 15 cc. of cold water (one mole of each) a precipitate formed at once. This dissolved completely when the mixture was well stirred. When the solution was heated to 80° it gave an amorphous precipitate that changed to microscopic crystals. After two hours of stirring these were filtered out, washed, dried and analyzed. Sarkar's iodate is given the formula Eu(IO<sub>3</sub>)<sub>3</sub>·5<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O. The results found here indicate four molecules of water.

The methods of preparation varied according to the nature of the acid and of the resulting salt. The formate, acetate, propionate, monochloro-

acetate, trichloroacetate, furoate, picrate, *p*-toluenesulfonate and *m*-nitrobenzenesulfonate were made by dissolving europium oxide in a hot aqueous solution of acid. These salts were all more soluble in hot than in cold water and crystallized well when their solutions were cooled.

The acetates of the cerium group of rare earths differ from europium acetate in having three molecules of water instead of four and in being less soluble in hot than in cold water.

Solutions of the sodium salts of the acids were treated with a solution of europium acetate or nitrate to prepare the maleate and fumarate. These salts are not much soluble in water. The former is soluble in cold dilute acetic acid. Other salts more or less difficultly soluble in water including the malonate, succinate, lactate, tartrate, pyruvate, citrate, benzoate, salicylate, cinnamate, benzilate, and basic sulfite could be made from a solution of europium acetate and the corresponding acid.

In several cases the salt did not separate at once but came down slowly when its solution was stirred and heated. This was true of the malonate, maleate, pyruvate, salicylate, lactate, citrate, acid tartrate and basic sulfite.

In general the salt, after its precipitation or crystallization, was filtered and washed well with water if it contained any foreign substance and afterward with methanol. It was dried in air or in a desiccator as necessary.

In the analyses when no complication occurred, the salt was simply ignited to the oxide, Eu<sub>2</sub>O<sub>3</sub>. In other cases europium was precipitated as oxalate and the latter ignited. The bromate and iodate were treated with potassium iodide and the liberated iodine titrated with thiosulfate. The sulfite could be titrated directly with iodine.

Several other europic salts were made which were not analyzed either because they were extremely deliquescent, as the perchlorate, dichloroacetate, bromide and sulfamate or of doubtful purity or interest as *o*-chlorobenzoate, *p*-bromobenzoate, naphthol-6-sulfonate, fluosilicate, hypophosphate and chromate. In addition there were made a number of very definite and interesting europous salts which have not yet been obtained

(1) Demarçay, *Compt. rend.*, **130**, 1469 (1900); **132**, 1484 (1901).

(2) Sarkar, *Bull. soc. chim.*, [4] **41**, 185 (1927).

(3) Urbain and Lacombe, *Compt. rend.*, **138**, 627 (1904).

(4) Urbain, *J. chim. phys.*, **4**, 31, 105, 232 (1906).

(5) Burion, *Compt. rend.*, **148**, 170 (1909).

(6) James and Robinson, *THIS JOURNAL*, **35**, 754 (1913).

(7) Katz and James, *ibid.*, **35**, 872 (1913).

(8) Urbain and Burion, *Compt. rend.*, **153**, 1155 (1911).

(9) Jantsch, Alber and Grubitsch, *Monatsh.*, **53-54**, 305 (1929).

(10) Yntema, *THIS JOURNAL*, **52**, 2782 (1930).

(11) McCoy, *ibid.*, **58**, 1577, 2279 (1936).

(12) Baxter and Tuemmler, *ibid.*, **60**, 602 (1938).

TABLE I  
 SALTS OF TRIVALENT EUROPIUM: EUROPIC SALTS

Salt	Formula	% Eu <sub>2</sub> O <sub>3</sub>		
		Calcd.	Found	Found
Formate <sup>6</sup>	Eu(HCO <sub>2</sub> ) <sub>3</sub>	61.32	60.97	
Acetate <sup>2</sup>	Eu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	43.89	43.91	
Propionate	Eu(C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	43.24	43.19	42.87
Oxalate <sup>2</sup>	Eu <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·10H <sub>2</sub> O	47.05	47.15	47.12
Malonate	Eu <sub>2</sub> (C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	49.02	48.96	
Succinate	Eu <sub>2</sub> (C <sub>4</sub> H <sub>4</sub> O <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	48.62	48.13	
Lactate	Eu(C <sub>3</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	38.59	38.47	38.56
Tartrate <sup>2</sup>	EuH(C <sub>4</sub> H <sub>5</sub> O <sub>6</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	36.14	35.81	35.71
Maleate	Eu <sub>2</sub> (C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	49.02	49.16	
Fumarate	Eu <sub>2</sub> (C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	49.02	48.44	
Monochloroacetate	Eu(C <sub>2</sub> H <sub>2</sub> ClO <sub>2</sub> ) <sub>3</sub> ·H <sub>2</sub> O	39.04	39.04	39.08
Trichloroacetate	Eu(C <sub>2</sub> Cl <sub>3</sub> O <sub>2</sub> ) <sub>3</sub> ·H <sub>2</sub> O	26.77	26.73	26.63
Pyruvate	Eu(C <sub>3</sub> H <sub>3</sub> O <sub>3</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	32.65	32.89	32.93
Citrate	EuC <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·4H <sub>2</sub> O	42.61	42.45	42.45
Furoate	Eu(C <sub>6</sub> H <sub>3</sub> O <sub>3</sub> ) <sub>3</sub> ·7H <sub>2</sub> O	28.81	28.95	29.00
Benzoate	Eu(C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	31.94	32.05	31.86
Picrate	Eu(C <sub>6</sub> H <sub>2</sub> N <sub>3</sub> O <sub>7</sub> ) <sub>3</sub> ·18H <sub>2</sub> O	15.17	15.12	15.19
Salicylate	Eu(C <sub>7</sub> H <sub>5</sub> O <sub>3</sub> ) <sub>3</sub> ·H <sub>2</sub> O	30.29	30.38	30.26
Cinnamate	Eu(C <sub>9</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>3</sub>	29.67	29.72	29.75
Benzilate	Eu(C <sub>14</sub> H <sub>11</sub> O <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	19.50	19.52	19.46
<i>m</i> -Nitrobenzenesulfonate	Eu(C <sub>6</sub> H <sub>4</sub> NSO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	20.32	20.51	20.19
<i>p</i> -Toluenesulfonate	Eu(C <sub>7</sub> H <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> ·8H <sub>2</sub> O	21.75	21.86	21.85
Basic sulfite	EuOHSO <sub>3</sub> ·4H <sub>2</sub> O	54.83	54.83	
Iodate	Eu(IO <sub>3</sub> ) <sub>3</sub> ·4H <sub>2</sub> O	SO <sub>2</sub> , 19.93	19.86	
			23.50	23.37
		IO <sub>3</sub> , 70.10	69.73	
Carbonate	Eu <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·3H <sub>2</sub> O	65.42	65.68	

entirely free from europic salts. These include the carbonate, oxalate, succinate, etc.

The fluoride, little soluble in water, oxidizes so fast in air that it sets fire to the filter paper after it has been washed with methanol.

**Analysis of Europous Salts.**—Soluble europous salts are quickly oxidized in air. The less soluble they are in water, the greater their permanence in air. Europous sulfate, EuSO<sub>4</sub>, is the most stable so far found. It suffers little change in the course of a year. This very small solubility makes its titration with permanganate very slow and the results uncertain. A completely satisfactory procedure was found in the addition of ferric sulfate prior to the titration. The latter reacts quickly and quantitatively with the europous salt to form soluble europic sulfate and ferrous sulfate. Titration of the latter follows the well-known method with permanganate. Ten cc. of a solution containing 0.5 g. of ferric sulfate and 5 g. of sulfuric acid were used for 0.3 to 0.4 g. of europous sulfate.

This method of analysis was tried with a fresh lot of europous sulfate. Twenty-five cc. of purest europium chloride, of density 1.14, was reduced in a reductor containing 400 g. of ten-mesh amalgamated zinc and run slowly into 150 cc. of a solution containing 25 cc. of 6 *N* hydrochloric acid and 15 cc. of 6 *N* sulfuric acid at 40 to 50°. The β form of europous sulfate resulted. It was filtered, washed with water and methanol, dried at 150° for one hour and titrated. Calcd. for EuSO<sub>4</sub>: Eu, 61.27. Found: Eu, 61.02, 61.06, corresponding to a purity of 99.54 and 99.62%.

The new volumetric method is also useful in the analysis of other europous compounds.

### Summary

A number of europic salts have been made and analyzed. An improved method of titration of europous salts is described.

PRIVATE LABORATORY  
1226 WESTCHESTER PLACE  
LOS ANGELES, CALIF.

RECEIVED JUNE 16, 1939