Cerous Citrate Complexes, their Composition, Structure and Behavior

BY M. BOBTELSKY AND B. GRAUS

The phenomena observed in this investigation may be accounted for as follows: a soluble anion complex of the composition $[CeCi_2]^{3-}$ ($pH \sim 6.0$) is formed in water and in 50% alcoholic solutions. Another soluble anion complex of the composition $[Ce_2Ci_3]^{3-}$ ($pH \sim 5.5$) is formed in water solution. $[CeCi_2]^{3-}$ and $[Ce_2Ci_3]^{3-}$ are precipitated quantitatively by cerous ion forming the insoluble $[CeCi]^0_n$ which is dissolved by sodium hydroxide giving the soluble anion $[CeCi']^{n-}_n$. $[Ce_2Ci_3']^{6-}$ is formed at $\geq pH$ 9.5. By addition of cerous ion to the latter, $[Ce_3Ci_3']^{3-}$ (or $[CeCi']^{1-}$) is obtained, which precipitates by addition of one more cerous ion, as $[Ce_4Ci_3']^0$ or $Ce[CeCi']^n_n$ ($pH \sim 7.0$).

The citrate complexes of the rare earth elements are used for the separation of these elements from one another.[1,2] Indication of the existence of several complex compounds in solutions which contain sodium citrate and $LaCl_3$ or $NdCl_3$ has been presented.[3] However, knowledge of the composition, structure and stability of the various citrate complexes of the rare earths, especially at high pH's, is incomplete. Our study of cerous was extended to basic, neutral and acid solutions. An extensive use was made of the "heterometric" method[4] ($=$ photometric measurements of suspension) which was developed in the past few years by the first author with co-workers. In addition, other physical methods were used.

It is remarkable that the composition and, probably, the structure of cerous and thorium citrate complexes (see report on thorium citrates) are very similar, although these elements are in different valency states.

Experimental

Reagents and Solutions.—Standard solutions of cerous nitrate and of sodium citrate were prepared by weighing the salts $Ce(NO_3)_3 \cdot 6H_2O$ (B. D. H. Laboratory Reagent, low in other rare earths) and $Na_3C_6H_5O_7 \cdot 2H_2O$ (C.P. J. T. Baker Analyzed).

Apparatus and Procedure.—Heterometric titrations were carried out using a "Heterometer" constructed by M. Bobtelsky for the study of reactions in a heterogeneous system. A description of the Heterometer and the procedure involved in heterometric titrations has been given in previous papers.[4] pH and conductivity titrations (at $25 \pm 0.1°$) were carried out parallel to the heterometric titrations. All heterometric and pH titrations were made at room temperature (18–27°).

Results and Discussion

Heterometric Measurements.—Figures 1 and 2 present the composition and results of titrations of solutions of cerous nitrate with sodium citrate and
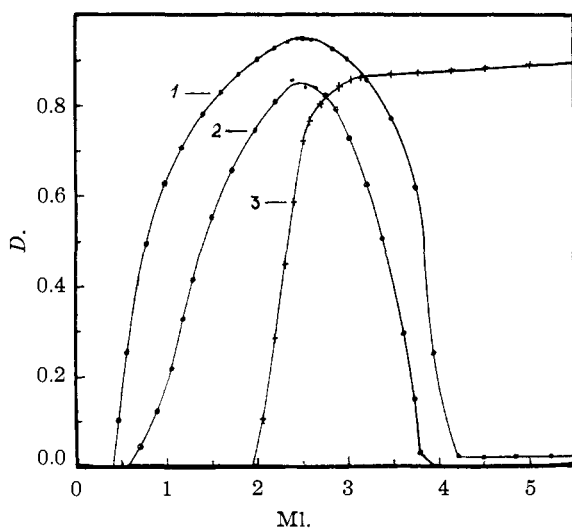

Fig. 1.—1, 5 cc. 0.1 M $Ce(NO_3)_3$ + 15 cc. H_2O + x cc. 0.2 M Na_3Ci; 2, 5 cc. 0.05 M $Ce(NO_3)_3$ + 15 cc. H_2O + x cc. 0.1 M Na_3Ci; 3, 3 cc. 0.1 M Na_3Ci + 17 cc. H_2O + x cc. 0.1 M $Ce(NO_3)_3$.

(1) F. H. Spedding, et al., THIS JOURNAL, **69**, 2777, 2786, 2812 (1947); ibid., **70**, 1671 (1950); W. C. Johnson, L. L. Quill and F. Daniels, Chem. Eng. News, **25**, 2494 (1947); E. R. Tompkins, J. X. Khyn and W. E. Cohn, THIS JOURNAL, **69**, 2769 (1947); D. H. Harris and E. R. Tompkins, ibid., **69**, 2792 (1947); D. I. Ryabshikov and E. A. Terent'eva, C. A., **43**, 49693 (1949).

(2) E. R. Tompkins and S. W. Mayer, THIS JOURNAL, **69**, 2859 (1947).

(3) A. D. Tevebaugh, C. A., **45**, 6952i (1951).

(4) M. Bobtelsky and B. Graus, THIS JOURNAL, **75**, 4172 (1953); ibid., **76**, 1536 (1954); M. Bobtelsky and B. Graus, Bul. Res. Council of Israel, **3**, 82 (1953); Anal. Chim. Acta,**9**,163 (1953); M. Bobtelsky and I. Bar-Gadda, Bull. soc. chim. France, **20**, 276, 382, 687, 819 (1953); Anal. Chim. Acta, **9**, 168, 446, 525 (1953); M. Bobtelsky and Y. Welwart, ibid., **9**, 281, 374 (1953); **10**, 151,156, 459, 464 (1954); N. Bobtelsky and M. Bihler, ibid., **10**, 260 (1954); M. Bobtelsky and M. Halpern, ibid., **11**, 84, 188 (1954); M. Bobtelsky and S. Kertes, J. App. Chem., **4**, 419 (1954).
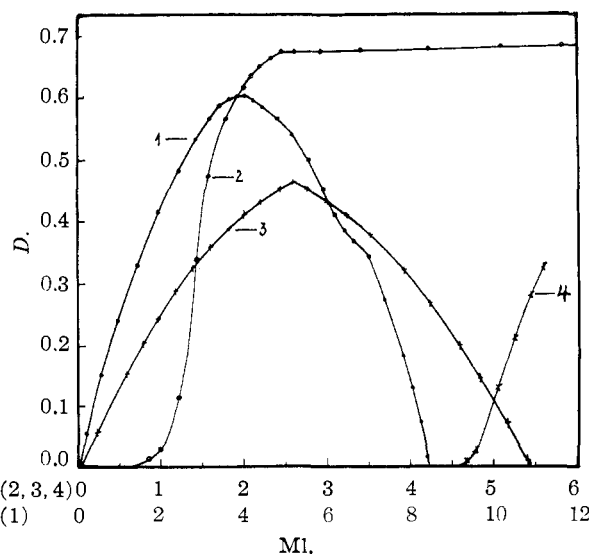
Fig. 2.—1, 7.5 cc. 0.05 M $Ce(NO_3)_3$ + 2.5 cc. H_2O + 10 cc. alc. + x cc. 0.1 M Na_3Ci 50% alc.; 2, 5 cc. 0.1 M Na_3Ci + 5 cc. H_2O + 10 cc. alc. + x cc. 0.2 M $Ce(NO_3)_3$; 3, 5 cc. 0.05 M $Ce(NO_3)_3$ + 5 cc. H_2O + 10 cc. alc. + x cc. 0.1 M Na_3Ci 50% alc.; 4, 5 cc. 0.1 M Na_3Ci + 5 cc. H_2O + 10 cc. alc. + x cc. 0.05 M $Ce(NO_3)_3$ 50 alc.

TABLE I

General composition: a cc. 0.1 M Na₃Ci + b cc. 0.1 M NaOH + (20 − a − b) cc. H₂O + X cc. 0.1 M Ce(NO₃)₃.

| Curve no. | NaOH, cc. (1) | Na₃Ci, cc. (2) | Measured cc. cerous | | Ce₂Ci₃ (5) | CeCi₂ (6) | Calcd. cc. cerous soluble as | CeCi' + CeCi₂ (8) | CeCi (9) | Calcd. cc. cerous as insoluble |
			At begin. of precip. (3)	At end of precip. (4)			CeCi' + Ce₂Ci₃ (7)			Ce₄Ci₃' + CeCi (10)
1	3	3.5	3.3	4.5	2.4	1.75	3 + 0.33 = 3.33	3.25	3.5	4 + 0.5 = 4.5
2	5	6	6	7.5	4	3	5 + 0.7 = 5.7	5.5	6	6.7 + 1 = 7.7
3	7.5	8	8.4	10	5.3	4	7.5 + 0.3 = 7.8	7.25	8	10 + 0.5 = 10.5
5	5	8	7	9.4	5.3	4	5 + 2 = 7	6.5	8	6.7 + 3 = 9.7
6	3	6	5	7.2	4	3	3 + 2 = 5	4.5	6	7

reverse titrations in water (Fig. 1) and 50% alcoholic solutions (Fig. 2).

In the direct titrations the point of the maximum optical density lies at the molar ratio of 1[Ce] : 1[Ci] (= [Ce-Ci]$_n$). On further addition of citrate the precipitate redissolves at the approximate ratio of 2[Ce] : 3[Ci] (= [Ce₂Ci₃]³⁻) (in water) or 1[Ce] : 2[Ci] (= [CeCi₂]³⁻) (in 50% alcohol). In the reverse titrations (Fig. 1, curve 3 and Fig. 2, curves 2 and 4) the same molar ratios are obtained at the points of initial precipitation. On examining the branch of solution in curve 1 (Fig. 2), we find a break at about the molar ratio of 2[Ce] : 3[Ci] which indicates that an intermediate compound (= [Ce₂Ci₃]³⁻) may be formed before the final soluble complex [CeCi₂]³⁻ is obtained.

The different molar ratios at which the initial precipitation occurs in water and in 50% alcoholic solution may be explained by the different solubility products of the same compounds in each of the solvents. In 50% alcoholic solution both [Ce₂Ci₃]³⁻ (as Na₃Ce₂Ci₃) and [CeCi]⁰$_n$ are insoluble, while in water solution only the latter is insoluble.

Whether the insoluble salts Ce[CeCi₂] and Ce[Ce₂Ci₃] both exist cannot be determined definitely, since they have the same empirical formula [CeCi]$_n$.

Experiments were carried out (Fig. 3) to study the behavior of the compounds ([CeCi]$_n$ ↓ and [Ce₂Ci₃]³⁻ ↑) obtained toward alkali. Curve 2 shows that the addition of sodium hydroxide has no perceptible influence on the soluble anion complex [Ce₂Ci₃]³⁻. A suspension of [CeCi]⁰$_n$ (curve 1) is completely redissolved by sodium hydroxide at the molar ratio of ≤ 1[OH⁻] : 1[Ci] (or ≤ 1[OH⁻] : 1[Ce]), probably by the neutralization of one hydrogen ion per one citrate. (The pH titration (Fig. 5) shows that the possibility of the precipitation of cerous hydroxide is excluded.)

A series of titrations were carried out by the addition of Ce(NO₃)₃ to alkaline citrate solutions (Table I). In all titrations the optical density remained unchanged at first. At a certain point which was close to the molar ratio of 1[Ce] : 1[Ci] an initial precipitation occurred. The density rose steeply and linearly until the first maximum density point was reached. On further addition of cerous a horizontal density line was obtained.

Stoichiometric calculations were made for the partial reactions proceeding in solution and the results are compiled in Table I. The calculations were made on the basis of the reactions which occur before and during the precipitation. As the table shows, the amount of cerous required in every

titration to obtain the maximum optical density (= complete precipitation) agrees without any exception with the calculated sum of the partial reactions (compare columns 4 and 10). In addition, if we compare the amounts of cerous measured at the beginning of the precipitation to those calculated on the assumption that [CeCi']¹⁻ + [Ce₂Ci₃]³⁻ (Ci' = Ci³⁻ minus one hydrogen) are obtained in the solution (compare columns 3 and 7), we see that they are in close agreement. The results are entirely different if we assume that no neutralization of Ci to Ci' occurs in solution (compare column 3 with columns 5 or 6).
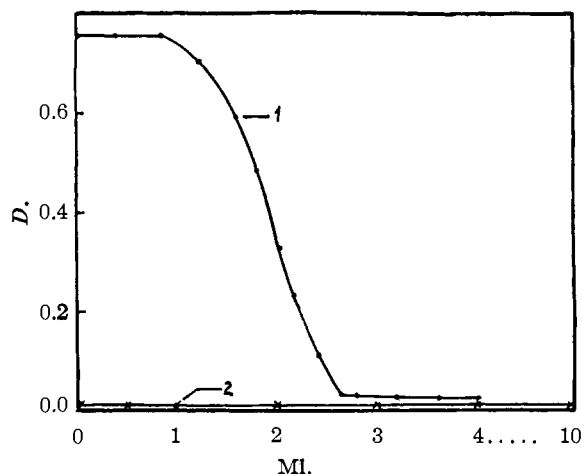

Fig. 3.—1, 3 cc. 0.1 M Ce(NO₃)₃ + 3 cc. 0.1 M Na₃Ci + 14 cc. H₂O + x cc. 0.1 M NaOH (red filter); 2, 3 cc. 0.1 M Ce(NO₃)₃ + 5 cc. 0.1 M Na₃Ci + 12 cc. H₂O + x cc. 0.1 M NaOH (red filter).

The reactions which occur in neutral and basic solutions may be accounted for as follows: in *neutral* solutions of cerous, which contain a sufficient quantity of sodium citrate, the soluble anion complex [Ce₂Ci₃]³⁻ is quantitatively formed according to the reaction (1)

$$2Ce^{3+} + 3Ci^{3-} \rightleftharpoons [Ce_2Ci_3]^{3-}\uparrow \qquad (1)$$
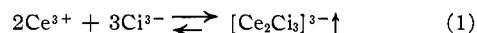
The anion complex may then be transformed by further addition of sodium citrate into the soluble anion complex [CeCi₂]³⁻ according to reaction (1a)
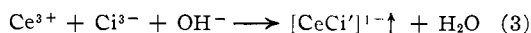
$$[Ce_2Ci_3]^{3-} + Ci^{3-} \rightleftharpoons 2[CeCi_2]^{3-} \qquad (1a)$$
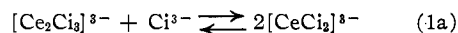
In water solution [Ce₂Ci₃]³⁻ is quantitatively precipitated by the addition of cerous according to reaction (2)

$$[Ce_2Ci_3]^{3-} + Ce^{3+} \rightleftharpoons [CeCi]^0{}_n\downarrow \text{ (or Ce[Ce}_2Ci_3]\downarrow) \qquad (2)$$
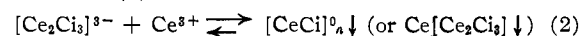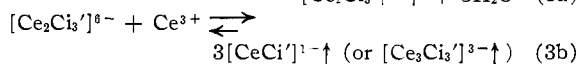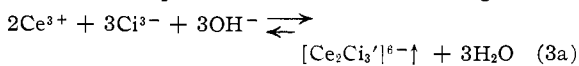
On the addition of cerous to a solution which con-

tains sodium citrate and sufficient NaOH, the partial reactions which occur may be summarized in one reaction as

$$Ce^{3+} + Ci^{3-} + OH^- \longrightarrow [CeCi']^{1-}\uparrow + H_2O \quad (3)$$

(Actually as the pH curve (Fig. 5, curve 1) shows, this reaction proceeds at least in two stages as

$$2Ce^{3+} + 3Ci^{3-} + 3OH^- \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}}$$
$$[Ce_2Ci_3']^{6-}\uparrow + 3H_2O \quad (3a)$$
$$[Ce_2Ci_3']^{6-} + Ce^{3+} \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}}$$
$$3[CeCi']^{1-}\uparrow \text{ (or } [Ce_3Ci_3']^{3-}\uparrow) \quad (3b)$$

If free sodium citrate remains in solution the excess cerous reacts with the citrate according to equation 1. When these reactions are completed, a further addition of cerous precipitates the salts
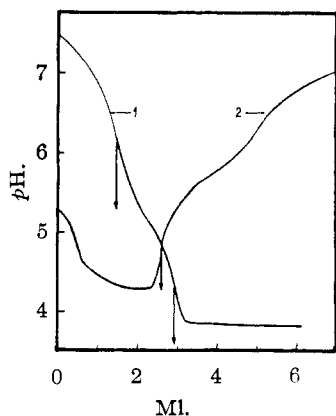

Fig. 4.—1, 3 cc. 0.1 M Na₃Ci + 17 cc. H₂O + x cc. 0.1 M Ce(NO₃)₃; 2, 5 cc. 0.1 M Ce(NO₃)₃ + 15 cc. H₂O + x cc. 0.2 M Na₃Ci.
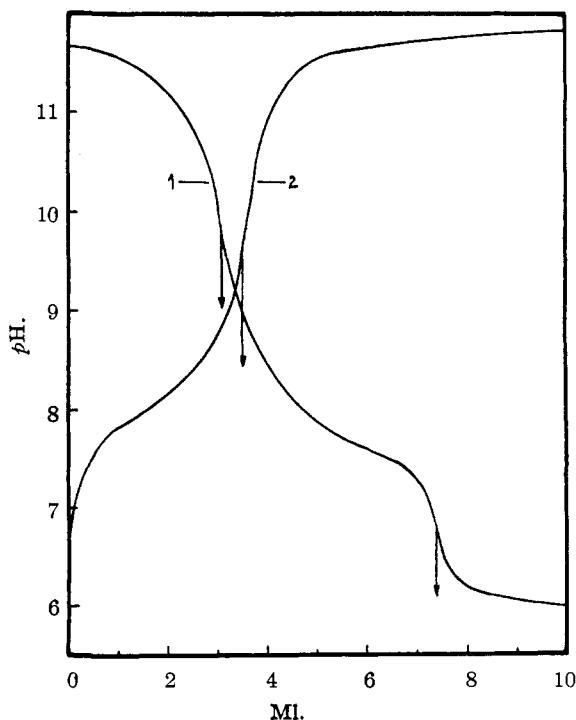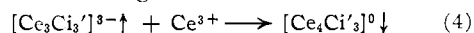

Fig. 5.—1, 6 cc. 0.1 M Na₃Ci + 5 cc. 0.1 M NaOH + 9 cc. H₂O + x cc. 0.1 M Ce(NO₃)₃; 2, 5 cc. 0.1 M Ce(NO₃)₃ + 6 cc. 0.2 M Na₃Ci + 9 cc. H₂O + x cc. 0.2 M NaOH.

$[CeCi]^0{}_n \downarrow$ and $[Ce_4Ci_3']^0 \downarrow$ according to reactions (2) and the following

$$[Ce_3Ci_3']^{3-}\uparrow + Ce^{3+} \longrightarrow [Ce_4Ci'_3]^0\downarrow \quad (4)$$

pH Measurements.—Figures 4 (neutral solution) and 5 (basic solutions) show the composition and results of pH titrations which are parallel to the heterometric titrations. The cerous ion, when added to a neutral citrate solution (Fig. 4, curve 1) gives two pH inflection points at pH $\geqslant$ 6.0 (= 1-[Ce]:2[Ci]) and at pH $\leqslant$ 4.5 (= 1[Ce]:1[Ci]). Sodium citrate when added to cerous solution (curve 2) gives one clear pH inflection point at
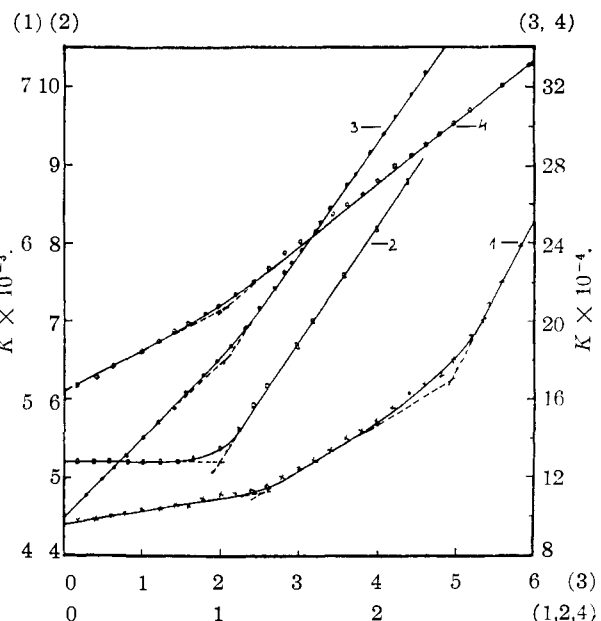

Fig. 6.—1, 5 cc. 0.1 M Na₃Ci + 45 cc. H₂O + x cc. 0.2 M Ce(NO₃)₃; 2, 5 cc. 0.1 M Ce(NO₃)₃ + 45 cc. H₂O + x cc. 0.5 M Na₃Ci; 3, 5 cc. 0.1 M Na₃Ci + 20 cc. H₂O + 25 cc. alc. + x cc. 0.2 M Ce(NO₃)₃; 4, 5 cc. 0.1 M Ce(NO₃)₃ + 20 cc. H₂O + 25 cc. alc. + x cc. 0.5 M Na₃Ci.
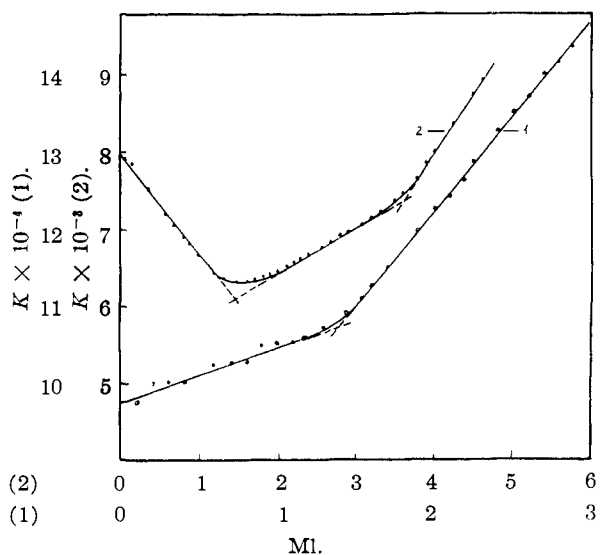

Fig. 7.—1, 5 cc. 0.1 M Ce(NO₃)₃ + 6 cc. 0.2 M Na₃Ci + 39 cc. H₂O + x cc. 0.5 M NaOH; 2, 6·cc. 0.1 M Na₃Ci + 5 cc. 0.1 M NaOH + 39 cc. H₂O + x cc. 0.2 M Ce(NO₃)₃.

pH $\sim$ 5.0 (1[Ce]:1[Ci]). Another pH inflection point may exist at pH $\sim$ 6.5 (= 1[Ce]:2[Ci]).

The changes in pH in the presence of sodium hydroxide (compare Figs. 3 and 4), are presented in Fig. 5. In curve 1, from the beginning (pH $\sim$ 11.7) the pH falls and two inflection points are obtained; the upper one lies at pH $\sim$ 9.5 at the molar ratio of 2[Ce]:3[OH$^-$] (= [Ce$_2$Ci$_3$']$^{6-}$) and the lower at pH $\sim$ 6.7. The latter occurs at a point when all the citrate is precipitated either as [Ce$_4$Ci$_3$']^0 or [CeCi]^0_n (equal to the calculated sum of both). Curve 2 shows the results of a titration of the anion complex with sodium hydroxide. The initial pH (= 6.7) rises and a pH inflection point occurs at pH $\sim$ 9.5 at which point the complex [Ce$_2$Ci$_3$']$^{6-}$ is quantitatively obtained. The anion complex which is neutralized by NaOH behaves like a weak monobasic acid (pK = 8.1).

Conductometric Titrations.—Titrations both in neutral (Fig. 6) and basic (Fig. 7) solutions were carried out. In the former, breaks were obtained at the molar ratio of 1[Ce]:2[Ci] and 1[Ce]:1[Ci] (curve 1). On the addition of NaOH to the anion complex (Fig. 7, curve 1) only one break occurs at the molar ratio of 2[Ce]:3[OH$^-$] (= [Ce$_2$Ci$_3$']$^{6-}$). On the addition of cerous to an alkaline citrate solution (curve 2) the conductivity falls linearly since sodium hydroxide is used up at this stage. The first break occurs at the point of the quantitative formation of [Ce$_2$Ci$_3$']$^{6-}$. This second break is obtained at the end of the precipitation of [Ce$_4$Ci$_3$']^0 + [Ce Ci]^0_n.

All these results show that in alkaline solution two complexes exist: one is probably [Ce$_2$Ci$_3$']$^{6-}$ and the other has the empirical composition [CeCi']$_n{}^{n-}$. [CeCi'] $\uparrow$ is either a monomer or it may be formulated as [Ce$_3$Ci$_3$']$^{3-}$ $\uparrow$. [CeCi'] may be obtained from a suspension of [CeCi]$_n$ $\downarrow$ by the addition of *one* equivalent of NaOH per *one* [CeCi].

Now we turn to the different *insoluble* compounds which exist in weakly basic, neutral or weakly acid solutions. On addition of cerous to the solutions containing the complexes [Ce$_3$Ci$_3$']$^{3-}$ or [Ce Ci']$^{1-}$, [Ce$_2$Ci$_3$]$^{3-}$ or [CeCi$_2$]$^{3-}$, insoluble compounds which may be represented as the salts of the above anion complexes are formed. [Ce$_3$Ci$_3$']$^{3-}$ gives (in weakly alkaline solution) an insoluble compound of the empirical composition [Ce$_4$Ci$_3$'] $\downarrow$. [Ce$_2$Ci$_3$]$^{3-}$ and [CeCi$_2$]$^{3-}$ give at pH $\gtrless$ 7 an insoluble compound of the empirical composition [CeCi]^0_n $\downarrow$. The latter is either a *mono* or *poly*-mer. Both possibilities may exist depending on the pH and the experimental conditions during the

precipitation. In neutral or weak basic solutions, the polymer may be obtained, while in more acidic solutions the regular salt, which is a monomer, is obtained.

We will now consider the possible structures of the above compounds. None of the structures presented below can *alone* satisfactorily solve all the problems which arise in connection with the formation of the compounds obtained. It must be assumed that any single structure may, under appropriate conditions, easily be transformed into the other.

The different compounds obtained may be formulated in the following way
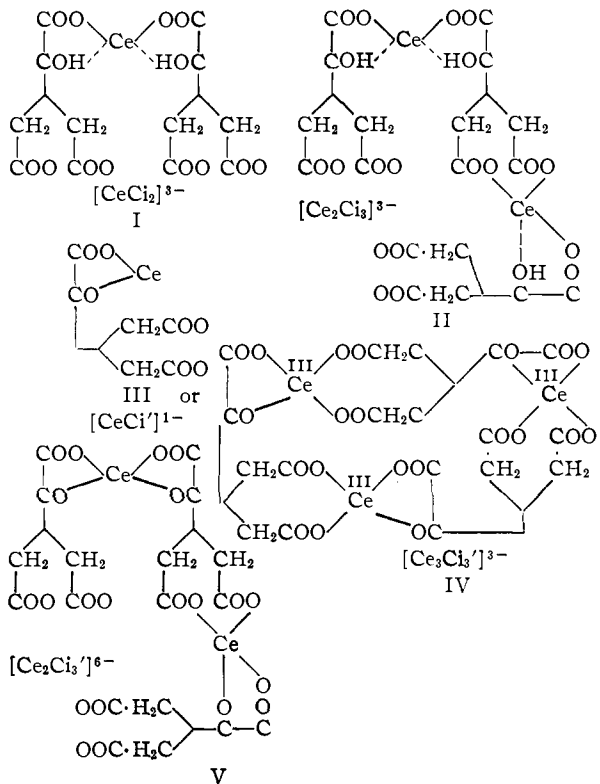
If we compare the composition and structures of cerous and thorium citrates we find striking similarities between them. The different valencies of the cations seems to be of no decisive influence, since their radii are approximately the same size. Generally the thorium complexes are obtained at lower pH's.

Jerusalem, Israel