On the Coprecipitation of Tetrapositive Ions with Lanthanum Fluoride

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Cunningham and Werner[1] in their first isolation of plutonium made use of the fact, first discovered by Seaborg, Wahl and Kennedy[2], that the lower oxidation states of Pu are coprecipitated with LaF_3 whereas the plutonyl ion PuO_2^{2+} is not. Pu could thus first be separated from the large amount of UO_2^{2+} originally present using LaF_3 as a carrier; then the Pu of the precipitate could be oxidized to PuO_2^{2+} and the La removed by a new precipitation. — The coprecipitation of Pu with La is believed to have also been used in the industrial production of Pu[3].

If Pu^{3+} coprecipitates with LaF_3 this is as could be expected. The ionic radii are very similar (La^{3+} 1.04 Å, Pu^{3+} 1.01 Å using Zachariasen's values[4] so we can expect a partial or even total replacement of the La^{3+} ions in LaF_3 by Pu^{3+}.

What is remarkable is, however, that *tetrapositive* plutonium is also carried almost quantitatively by LaF_3 under circumstances where PuF_4 would not precipitate in the absence of La. This coprecipitation is generally ascribed to adsorption[5]. On the other hand Cefola and Smith[6] analyzed a number of LaF_3-PuF_4 precipitates, prepared with an excess of Pu in the solution, and found that the ratio La^{III}: Pu^{IV} varied between 1.81 and 3.4. Their conclusion was that a compound $La_2PuF_{10}(H_2O)_x$ is formed. They do not seem to have used X-ray photographs.

We shall now give evidence supporting a third explanation, namely that solid solutions are formed, which are in this case anomalous mixed crystals.

One of us (KS) has made an extensive investigation of the coprecipitation with LaF_3 of trivalent lanthanide ions and of some tetravalent ions. Sodium fluoride solution was added to an acid solution containing La^{3+}, the other ion in question, and nitrate or sulfate ions. The precipitate was kept at 100° C for some time in order to get larger crystal grains. In some cases the samples were kept with the supernatant solution in an autoclave at 220° C. Finally the preparations were investigated by means of powder photographs using focussing cameras.

For the tripositive ions the results were qualitatively as expected. The ions of radii close to La^{3+} (La^{3+} 1.04 Å, Ce^{3+} 1.02 Å, Pr^{3+} 1.01 Å, Nd^{3+} 0.99 Å)[4] form fluorides MF_3 isomorphous with LaF_3; for these ions mixed crystals with the LaF_3 structure were obtained for all ratios $LaF_3 : MF_3$.

For lanthanides with shorter ionic radii, MF_3 is not isomorphous with LaF_3. However, a range of solid solutions were found extending from pure LaF_3 to a certain percentage of MF_3, decreasing with the radius of M^{3+}.

Experiments were also made with the tetrapositive ions Th^{4+} (0.95 Å), U^{4+} (0.89 Å) and Ce^{4+} (0.87 Å). The two latter ions have radii close to that of Pu^{4+} (0.86 Å) whereas Th^{4+} is larger[4].

From both $Ce^{4+}-La^{3+}$ and $U^{4+}-La^{3+}$ solutions predipitates could be obtained with the LaF_3 structure but with lattice dimensions considerably smaller than those of pure LaF_3. (For high percentages of MF_4, other phases appeared as well.) Some preliminary figures for the hexagonal *a* and *c* axes of these preparations are given in Fig. 1, and compared with those of pure LaF_3 and CeF_3. The circles give

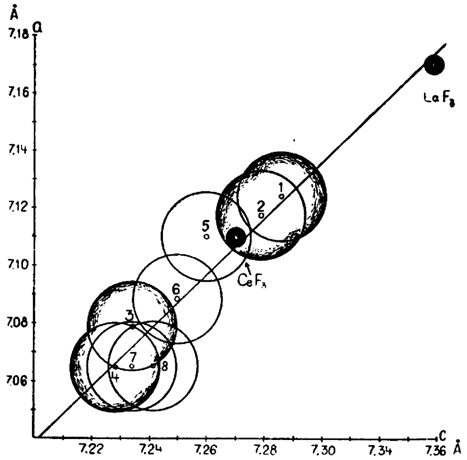

Fig. 1. a and c axes of phases with the pure LaF_3 *structure: pure* LaF_3 *and pure* CeF_3 *(small circles),* $La^{3+}-U^{4+}$ *fluorides (large open circles 5—8) and* $La^{4+}-Ce^{4+}$ *fluorides (large shaded circles 1—4). The original mole percentage in the solution increases from 11.0 %* Ce^{4+} *in 1 to 44.0 %* Ce^{4+} *in 4 and from 14.7 %* U^{4+} *in 5 to 35.5 in 7 and 44.9 in 8. These figures, however, do not give the real percentage of* U^{4+} *in the fluoride crystals since there has been some transformation to* Ce^{3+} *and* UO_2^{2+} *and some* M^{3+} *may remain in the solution. In samples 4, 7, and 8 other phases were also present.*

the estimated limits of error, which are much wider for the mixed crystals than for the pure compounds. This is because the latter could be recrystallized, CeF_3 by heating with the supernatant liquid to 220° C in an autoclave and LaF_3 even by heating in air to 400° C, so that their powder photographs gave very sharp lines. The same treatment of the $La^{3+}-Ce^{4+}$ and $La^{3+}-U^{4+}$ precipitates led to decomposition with the formation of Ce^{3+}, and of UO_2 and other products. Thus the measurements must be made on specimens recrystallized at only 100° C, which had slightly broader lines.

Obviously Ce and U must have entered the lattice in varying amounts. One might suggest that Ce had been reduced to Ce^{3+} and then entered the lattice; however the shrinking of the lattice is certainly larger than could be explained merely by the formation of mixed crystals LaF_3-CeF_3.

We thus conclude that the LaF_3 lattice really contains Ce^{4+} and U^{4+}.

The most plausible mechanism for the formation of the solid solutions seems to be a random replacement of La^{3+} by M^{4+} and "holes" in the ratio 4 La^{3+}: (3 M^{4+} + 1 hole), whereas the fluoride framework is not changed. (The replacement of 4 La^{3+} by 4 M^{4+} + 4 F^- in interstices of the lattice would require a widening rather than a shrinking of the cell dimentions.)

La^{3+} has previously been shown to enter anomalous mixed crystals with the CaF_2 structure, *e.g.* 1 La^{3+} + 1 F^- replacing 2 Sr^{2+} [7–11]. As far as we know, however, anomalous mixed crystals with the LaF_3 structure have not been demonstrated previously.

It seems overwhelmingly probable that Pu^{4+} with a radius close to those of Ce^{4+} and U^{4+} will behave in the same way as these ions and that the coprecipitation with LaF_3 is due to the formation fo solid solutions. Then the reaction used in the laboratory and technical process tends towards a real thermodynamic equilibrium and is not due to the somewhat capricious phenomenon of surface adsorption.

A more detailed account of these experiments will be published later on.

There are many other cases where precipitation on a carrier is used for practical preparation and purification purposes. It seems to us that it would also be desirable in other cases to investigate whether the process is due to surface adsorption, solid solution or compound formation since such knowledge would be a good guide in the choice of the best experimental conditions. Perhaps the formation

Studies in the Tropolone Series

II. Puberulonic Acid

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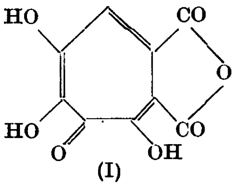
At the symposium on the chemistry of tropolones held by the Chemical Society in London on November 2nd 1950, various structural formulae for puberulonic acid[1] were discussed. The author wishes to record that she proposed, on that occasion, the anhydride structure (I) for this acid.



(I)

This suggestion was based upon a new potentiometric titration curve for the substance in combination with a detailed study of its ultra-violet absorption properties in various solvents and in aqueous solutions of different pH-values, and also upon the comparison with corresponding data for stipitatic and puberulic acids.

An investigation of the infra-red spectra of puberulonic acid as well as of several related compounds, carried out in collaboration with Professor H. Theorell at Medicinska Nobelinstitutet, Stockholm, strongly supports the above formula for puberulonic acid.

Full details of these investigations will be published shortly in this journal.

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of anomalous mixed crystals will prove to be a more common phenomenon than has hitherto been believed.

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