226. *Polynuclear Complexes of Lanthanon Sulphates.*

By R. C. Vickery.

The soluble complexes formed by interaction of lanthanon alkali sulphates with ammonium acetate are described and their application to rare-earth fractionation studied. It is shown that fractional decomposition of the complex gives a rapid separation of lanthanum. Fractional crystallisation is not thus applicable. A fluorescence test for neodymium is described.

A new principle of fractionating the rare earths by use of anion complexes has recently been demonstrated by Beck (*Helv. Chim. Acta*, 1946, **29**, 357; *Mikrochim. Acta*, 1948, **33**, 344) who employed the lanthanon nitrilotriacetate complexes with oxalic acid and fractionally precipitated them by gradually increasing the pH. A good separation of lanthanum was claimed and some separation of the other lanthanons was also observed; Beck did not however apply this work to the heavy lanthanons. Marsh (*J.*, 1950, 577) found that fractionation of the hexa-antipyrine lanthanon iodides presents a means of rapid separation of the heavy earths,

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* See also B.P. 615,006/1946.

in particular lutecium, and ascribes this to a large difference in complex formation, rather than to a difference in solubility. It thus appears that fractionation is based on the crystallisation of the compounds which form more strongly bound complexes. These are the more weakly basic and give slightly the less soluble complexes. Marsh's work is however based on the suggestion of Freed (*J. Amer. Chem. Soc.*, 1931, **53**, 3906) that non-solvated ions would permit better fractionation than occurs with solvated ions. In spite of the apparent confirmation of Freed's hypothesis it is nevertheless of interest further to consider the use of solvated complexes.

Urbain (*Bull. Soc. chim.*, 1896, [iii], **15**, 338, 347) showed that lanthanon alkali sulphates dissolve in ammonium acetate solution and we hoped that the usefulness of the double-sulphate fractionation might be enhanced by fractional crystallisation or decomposition of the complex salt thus formed. There appears to have been no previous work on these complexes of the rare earths; Britton and his co-workers (*J.*, 1926, 293; 1931, 2831; 1932, 183; 1933, 5) studied electrometrically some rare-earth acetate and tartrate systems, but their work had no application to the lanthanon double sulphate aceto-complexes.

Organic hydroxy-acid complexes of tervalent metals are generally of the inner complex type of the second order (Werner), but the stability of such complexes varies greatly and there is no strict division between inner complex, and double or triple salt formation. Ryabchikov and Terent'eva (*Izvest. Akad. Nauk. S.S.S.R., Otdel Khim. Nauk.*, 1949, 44) took as criteria of complex formation the absence of precipitation by fluoride, chromate, hydroxyl, and ferrocyanide, in this order of decreasing effectiveness, and found, *inter alia*, that with ammonium acetate, lanthanon nitrates give not very stable complexes of the form $(Ln_3OAc)(NO_3)_6,nH_2O$. On this basis it might be considered that the dissolution of lanthanon alkali sulphates in ammonium acetate might be due to the formation of similar sulphate complexes.

The double sulphate acetato-complexes can be obtained either by direct dissolution of the lanthanon alkali sulphate in ammonium acetate solution or by suspending the double sulphate in acetic acid and adding ammonia. The solution thus obtained is extremely unstable, being decomposed by all the ions suggested as reagents by the Russian workers, and by alcohols, ketones, and acids. Precipitation of the sulphate by barium chloride is immediate and complete, whilst precipitation of the lanthanons by oxalate although finally complete is not immediate—these reactions appear to indicate that the lanthanon is enclosed in an *inner*, weak shell of the complex, whilst the SO_4^- is in the outer shell. These considerations are in conformity with the Russian work.

Crystallisation of the complex from the aqueous solution is not easy owing to the presence in the solution of sodium sulphate and excess of ammonium acetate, as well as to the tendency of the solutions to become supersaturated. Attempts were made to prepare the complex without the presence of excess of ammonium acetate, by employing an excess of the double sulphate which was filtered off before crystallisation. This technique was, however, not effective as an excess of acetate over that required for formation of the complex appears to be required in solution.

When finally isolated, the complex formed hexagonal prisms of the composition: Ln_2O_3, 39·1; SO_4^{--}, 37·3; NH_4^+, 6·8; $CH_3{\cdot}CO_2$, 22·9; equivalent to $Ln[Ln(OAc)_3(NH_4)_3](SO_4)_3$, which requires Ln_2O_3, 38·6; SO_4, 37·5; NH_4, 7·0; $CH_3{\cdot}CO_2$, 23·1%.

The 6-co-ordination of the lanthanons is well shown in this compound, and its stability apparently depends on maintenance of both ammonium and acetate ions in the inner shell; displacement of the acetate ion by addition of a mineral acid decomposes the complex, with re-formation of lanthanon sulphate and consequent precipitation of the double alkali sulphate. If the pure complex is employed for this decomposition, the precipitate is that of the lanthanon ammonium sulphate; if however the initial solution of double alkali sulphate is decomposed, the appropriate lanthanon alkali sulphate is obtained without ammonium sulphate.

The hydration of the complex shows great variation—2, 5, 9, 11, and 16 moles of water have been found under various conditions. The analyses of the complex given above have therefore been related to the anhydrous compound.

In attempts to crystallise a mixed lanthanon complex, little differentiation is obtained. The more basic lanthanons do not so readily retain the complex structure and rapidly revert to double sulphates which contaminate the complex crystals. Further, neodymium salts tend to be deposited as basic tetra-acetate on prolonged crystallisation, and this too contaminates the product. The lanthanons thus cannot be effectively separated by fractional crystallisation of this complex. For the preparation of the characteristic compound, samarium is best used: it is neither too basic for ready decomposition nor is its atomic number so high that precipitation as double alkali sulphate is prevented.

As pointed out above, decomposition of the complex is easily accomplished by the addition of mineral acids. It is not possible, even empirically, to calculate the equivalent of acid required for the decomposition of the complex but any desired number of fractions can be obtained by varying the quantity of acid added. By this means good separation of lanthanum is obtained from the light earths, as well as a reasonable separation of neodymium and praseodymium.

EXPERIMENTAL.

Throughout the present studies the lanthanon sodium sulphates used had the composition : Ln_2O_3, 44·5; SO_3, 43·0; H_2O, 5·0%, corresponding to $Ln_2(SO_4)_3,Na_2SO_4,2H_2O$, and the Ln_2O_3 was of the approximate composition La_2O_3, 40; Nd_2O_3, 45; Pr_6O_{11}, 12; Sm_2O_3, etc., 3%.

Lanthanon sodium sulphate (450 g.) was dissolved in a solution of ammonium acetate (1350 g.) in water (3·5 l.). This quantity of ammonium acetate was the minimum requirement found both by use of the solid salt and by its preparation *in situ* from acetic acid and ammonia solution. This solution, heated to 80° with mechanical stirring, was fractionally decomposed by the addition of sulphuric acid–water (1 : 1). Initially, 10-ml. quantities of the acid were added to effect decomposition and precipitation, the system being digested for 30 minutes before removal of the precipitate. Towards the end of the fractionation, however, it was necessary gradually to increase the volume of acid added to give a constant amount of precipitate. This might possibly be due to the formation of complexes of the lanthanon ammonium sulphates; these, being somewhat more soluble than the sodium salts, might be expected to require a higher acid concentration for decomposition. In spite of the attempts to attain equilibrium in the system by digestion, it was very difficult to keep the quantity of precipitate the same. Initially, precipitation required a certain period to elapse before it became evident, but with later fractions precipitation became more immediate, although, as indicated above, addition of more acid was necessary. It was never possible to get agreement between the quantity of acid added, the theoretical decomposition of ammonium acetate, and the quantity of precipitate.

Analyses of initial, intermediate and final fractions were :

Fraction.	Ln_2O_3, %.	SO_3, %.	H_2O, %.	Equiv. to :
2	44·5	43·8	2·5	$Ln_2(SO_4)_3,Na_2SO_4,H_2O$
11	44·5	43·1	5·2	$Ln_2(SO_4)_3,Na_2SO_4,2H_2O$
20	39·1	45·9	2·1	$Ln_2(SO_4)_3,Na_2SO_4,(NH_4)_2SO_4,H_2O$

The composition of the oxides was determined absorptiometrically in alternate fractions :

<table>
<tr><th>Fraction.</th><th>G.</th><th>Nd₂O₃, %.</th><th>Pr₆O₁₁, %.</th><th>Ln₂O₃, % (by diff.).</th></tr>
<tr><td>1</td><td>2·5</td><td>—</td><td>—</td><td>>99</td></tr>
<tr><td>2</td><td>10·5</td><td>—</td><td>—</td><td>>99</td></tr>
<tr><td>3</td><td>3·5</td><td colspan="2">1·0</td><td></td></tr>
<tr><td>4</td><td>6·5</td><td>—</td><td>—</td><td>>98</td></tr>
<tr><td>5</td><td>26·5</td><td colspan="2">2·0</td><td></td></tr>
<tr><td>6</td><td>14·5</td><td>—</td><td>—</td><td>>97</td></tr>
<tr><td>7</td><td>1·0</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td>8</td><td>2·0</td><td>62</td><td>25</td><td><i>ca.</i> 10</td></tr>
<tr><td>9</td><td>15·0</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td>10</td><td>3·0</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td>11</td><td>13·0</td><td>71</td><td>16</td><td><i>ca.</i> 10</td></tr>
<tr><td>12</td><td>3·0</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td>13</td><td>7·0</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td>14</td><td>5·0</td><td>81</td><td>15</td><td><i>ca.</i> 1</td></tr>
<tr><td>15</td><td>7·0</td><td></td><td></td><td></td></tr>
<tr><td>16</td><td>16·0</td><td>84</td><td>15</td><td>—</td></tr>
<tr><td>17</td><td>7·5</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td>18</td><td>1·5</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td>19</td><td>10·0</td><td>88</td><td>6</td><td>—</td></tr>
<tr><td>20</td><td>10·0</td><td>—</td><td>—</td><td>—</td></tr>
<tr><td>oxalate ppt.</td><td></td><td></td><td></td><td></td></tr>
<tr><td>21</td><td>5·0</td><td>73</td><td>5</td><td>—</td></tr>
</table>

These absorptiometrically determined figures cannot be assumed to be within ±2%, but they show the progress of fractionation.

Absorptiometric analysis was carried out with the usual "Spekker" instrument using 1-cm. cells and Ilford 604 filters with a mercury lamp. During these analyses a peculiar fluorescence effect was noted with Nd^{3+}-containing crystals or solutions : these exhibited a remarkably intense sky-blue fluorescence under light from a mercury lamp. The other lanthanons appeared not to interfere with, or mask, this fluorescence which can serve as a qualitative test for neodymium, down to about 5 mg. in 10 ml. of solution, or the appropriate concentration in crystals.

The rapid decomposition and removal of the lanthanum-containing complex from the system is only to be expected in view of the highly basic character of this element. The decrease in Nd_2O_3 content of the final oxides was undoubtedly caused by presence of a samarium concentrate : attempts to extract the samarium from this fraction by the method of Clifford and Beachell (*J. Amer. Chem. Soc.*, 1948, **70**, 2730) were not successful, but Marsh's sodium amalgam method yielded 0·75 g. of a pure white oxide.

Further runs, with constant-boiling hydrochloric acid instead of sulphuric acid, gave similar results. One factor of importance to the separation was the concentration of Ln_2O_3. With a concentration of oxides greater than 10%, removal of lanthanum was poor and the general spreading of fractions weak. The optimum concentration would appear to be quite low—about 10—20 g. of Ln_2O_3 per l.—but in all the work hitherto carried out the concentration has only once been begun at this level and then exceptionally good and clean fractionation was obtained. At any concentration and with either acid, cerium whether in traces or substantial quantities was found to spread throughout the series.

Fractional crystallisation was attempted with a solution of 75 g. of double sulphate in a concentrated aqueous solution of 230 g. of ammonium acetate. The difficulties enumerated above were immediately encountered, but by perseverence the series was extended to twelve fractions, individual analyses of which showed complete inconsistency and lack of separation.

Attempts to prepare the individual complexes also met with difficulties. Pure lanthanum sodium sulphate was too basic to enter readily into solution in ammonium acetate, and the tervalent cerium salt likwise was difficult to incorporate into a complex; the quadrivalent salt was too unstable to handle; neodymium gave rise to many basic salts, but praseodymium and samarium gave complexes fairly readily and could be separated from excess of ammonium acetate by crystallisation from water although the praseodymium solutions showed a tendency to hydrolysis. Samarium solutions are normally stable for about a week, after which hydrolysis slowly sets in.

The samarium *complex* was prepared, crystallised from water, and dehydrated (Found: Sm_2O_3, 42·3; SO_3, 29·7; NH_3, 6·0; $CH_3{\cdot}CO_2$, 22·0%. $Sm[Sm(NH_4)_3(CH_3{\cdot}CO_2)_3](SO_4)_3$ requires Sm_2O_3, 42·6; SO_3, 29·3; NH_3, 6·22; $CH_3{\cdot}CO$: 21·6%).

Initial crystallisation of the complex gave hexagonal prisms, but after 3—4 crystallisations tabular plates were obtained, and analysis showed a basic salt to have been formed.

The prismatic crystals decompose when washed with alcohol and can be dried only over magnesium perchlorate. Desiccation over sulphuric acid leads to partial decomposition of the crystals. Attempts were made to define hydrate compositions, but even under controlled conditions wide variations were obtained although the ratios of lanthanon, sulphate, acetate, and ammonia remained constant.

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