421. *Separation of Lanthanons by Means of Complexes with Amino-acids.*

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The formation of complexes by amino-acids with the lanthanons affords an effective method of separating the lighter earths by oxalate fractionation but has little effect on the heavy lanthanons. Of the amino-acids studied, histidine forms the strongest complexes, glycine being less efficient; other amino-acids are of but little value. Rapid separation of lanthanum is obtained, as well as speedy concentration of samarium; some separation of praseodymium and neodymium is also observed. Indications have been found of the possible existence of two stages of co-ordination with the amino-acids, and some crystalline lanthanon–amino-acid complexes have been prepared and analysed.

RECENT developments in the chemical separation of the lanthanons depend upon the use of agents forming complexes of varying stability with these elements. Prandtl (*Z. anorg. Chem.,* 1922, **120,** 120, etc.) early showed the value of ammine groupings in lanthanon separations; Beck (*Helv. Chim. Acta,* 1946, **29,** 357) has utilised nitrilotriacetate complexes, and the author (*J.,* 1950, 1101) recently indicated the use of carboxylic as well as amino-groups in double sulphate fractionation. Marsh (*J.,* 1950, 1819) has since demonstrated the value of ethylenediamine-*NNN'N'*-tetra-acetic acid as co-ordinating agent in separations of both light and heavy lanthanon groups.

Schwarzenbach and his school (*Helv. Chim. Acta,* 1945, **28,** *et seq.*) found that ethylenedi-aminetetra-acetic acid and 1 : 2-diamino*cyclo*hexane-*NNN'N'*-tetra-acetic acid were the strongest co-ordinating agents for the alkaline earths and that the co-ordinating strengths of these agents held also for certain of the tervalent elements including lanthanum and cerium.

The structures necessary for formation of complexes of this type are summarized by Marsh (*loc. cit.*) as " one or more secondary or tertiary amino-groups, and two or more acetate radicals so disposed as to give rise to chelate structures." It would be expected therefore that the amino-acids might prove of value in the formation of complexes with the lanthanons. The co-ordinated compound of copper with glycine is well known and presents many analogies to that with ethylenediamine, so lanthanon–amino-acid compounds should show many features comparable with those of the ethylenediamine compounds and thus be useful for fractionation.

It might, moreover, be expected that the amino-acids should be of two-fold value, their " zwitterionic " characteristics rendering chelation possible at both ends of the molecule.

Ryabchikov and Terent'eva (*Izvest. Akad. Nauk. S.S.S.R., Otdel Khim. Nauk.*, 1949, 44) indicated that, of the amino-acids, glutamic and aspartic acids form the most stable complexes with lanthanons, and Pfeiffer (*Annalen*, 1933, **503**, 84; *J. pr. Chem.*, 1933, **136**, 321) showed that of the amino-acids, $NH_2 \cdot [CH_2]_n \cdot CO_2H$, those with $n = 1$ or 2, giving rise to 5- or 6-membered rings respectively, alone function as chelating groups.

According to Schmidt and Smythe (*J. Biol. Chem.*, 1930, **88**, 241) complexes should best be formed by amino-acids possessing a hydroxyl group in the α-position with respect to the carboxyl group and by the dicarboxylic amino-acids providing that no CH_2 groups interpose between the carboxyl groupings. It would be difficult to adhere to these criteria but it might reasonably be expected that co-ordination would be more likely the higher the concentrations of amino- and carboxylic groupings. The stability of the complex formed with cystine, however, is not so high as that with glycine, probably owing to the sulphur atoms present in the molecule.

Comparative stability constants have been given by Maley and Mellor (*Nature*, 1948, **161**, 437; 1950, **165**, 453; *Australian J. Sci. Res.*, 1949, *A*, **2**, 92) for ethylenediamine and amino-acid complexes of bivalent metal ions; Schwarzenbach (*loc. cit.*) gives pK values of 9·8 and 9·2 for lanthanum and cerium ethylenediamine compounds, respectively, and in this region the constants for histidine and ethylenediamine are quite comparable. Histidine apparently forms complexes more readily than do the other amino-acids, and Maley and Mellor suggest that this may be due to attachment by amino- and imino-groupings rather than the amino- and carboxyl groupings of other amino-acids—this is more or less confirmation of the assumption (see above) that it is the constitutional concentration of amino-groups which influences the co-ordinating strength. Apart from the degree of attachment of the co-ordinating group there is good reason to assume that basicity has much to do with the stability of individual lanthanon complexes— this is also indirectly stated by Irving and Williams (*Nature*, 1948, **162**, 746) : " the more stable the complex the lower the pH at which it can exist."

The use of amino-acids for forming complexes with the lanthanons appears confined from the practical aspect to glycine and histidine. Glutamic and aspartic acids and cystine, although apparently forming complexes to a small degree, are ineffective in aiding separation of the lanthanons—in this respect it has not been possible to confirm the Russian workers' results (*loc. cit.*) that glutamic and aspartic acids form the most stable complexes. Of all the amino-acids studied, histidine and glycine are the only ones to co-ordinate with lanthanon hydroxides in neutral or ammoniacal solutions. Ammoniacal solutions of the other amino-acids will not form complexes at all and require acidification in order to obtain solution. From these acid solutions only oxalate precipitation is practicable, and except with histidine and glycine separation was normally little better than ordinary oxalate precipitation, the lanthanum coming out at the tail in small yield but of good purity.

It would, however, appear that two types of co-ordination exist between the lanthanons and the amino-acids. If excess of lanthanon hydroxides is digested with aqueous glycine or histidine, and the solution filtered from excess of hydroxide, the lanthanon solution, on fractional precipitation with oxalic acid, separates in the normal sequence, *i.e.*, in inverse order of atomic number although with a somewhat enhanced separation. If, however, appreciable excess of amino-acid is employed for complete dissolution of the lanthanon hydroxides, then fractional oxalate precipitation will bring down the lanthanum at the head with the other earths following in order of atomic number, giving a degree of separation equivalent to that obtained by Marsh with ethylenediaminetetra-acetate. There thus appears to be a primary solvation effect with but little co-ordination, and a secondary fully co-ordinating effect. Possibly there exists an equilibrium in the first effect which depresses full co-ordination and this equilibrium is destroyed by the presence of excess of amino-acid. Since this effect has been noted with both glycine and histidine complexes, it cannot be ascribed to an antagonism between amino- and imino-groupings for complex-formation but might be a more general effect for hydroxides of high basicity, indicating antagonism between carboxyl and amino-groupings.

Such a hypothesis would explain the discrepancy of the degree of co-ordination found here with that given by the Russians, for if they obtained only the primary complex in some cases and full co-ordination in others, then their observations on the comparative stability of such complexes would be invalid.

Reversal of the oxalate series is in line with that obtained with ethylenediaminetetra-acetate and is probably indicative of full co-ordination.

With histidine as co-ordinating agent, fractional precipitation with oxalic acid enables good concentrations of lanthanum and samarium to be obtained at the head and tail of a short series. Table II shows that lanthanum increased from 40 to 95% in the first fraction and was absent after

the fourth; in six fractions samarium was increased from 5·0 to 50%; some separation of praseodymium and neodymium is also seen. Fractionation in the presence of glycine is not so effective (see Table I); increase of the number of fractions to eight gave a 90% lanthanum at the head with only the last two fractions free from this element (determined by spark spectroscopy); a 40% samarium concentrate was obtained at the tail but praseodymium and neodymium showed little separation.

Co-ordination should be greater with the heavy, less basic lanthanons, but very little separation could be obtained in this group in the presence of either histidine or glycine. Extension of the series to eighteen fractions gave a certain removal of erbium from the first half of the series, but apart from this negligible variations were obtained.

Fractionation as oxalates in the presence of histidine is probably as effective as with ethylenediaminetetra-acetic acid; amino-acids, however, cannot directly form complexes again with the precipitated oxalates, so continued fractionation by this means requires intermediate conversion into hydroxides before a series can be carried on. Nevertheless, the effectiveness of the method here described is further indication of the greatly enhanced separations obtained by the use of co-ordinating agents.

<div align="center">EXPERIMENTAL.</div>

Preliminary qualitative work showed that of all the amino-acids only aqueous solutions of histidine and glycine would form complexes with lanthanon hydroxides in neutral or ammoniacal solutions. In acid solutions all the amino-acids formed complexes but in such cases it was difficult to determine which had most effect, solvating action of the mineral acid or co-ordinating action of the amino-acid. Quantitative work was therefore only carried out with histidine and glycine.

Glycine Complexes : Separation of the Light Lanthanons.—The lanthanon hydroxides were derived from mixed sources but were approximately in the same ratio as in monazite minus cerium. 75 G. of hydroxide (65 g. of oxide) were treated with 440 ml. of 20% aqueous glycine with slight warming to give a faintly turbid solution. The turbidity could be cleared with one or two drops of hydrochloric acid but this addition appeared to alter the structure of crystals obtained from the solution. The neutral solution crystallised quite well, giving hexagonal, wurtzite-type crystals; the acidified solution yielded, however, well-formed octahedra.

After dissolution of the hydroxides a further 450 ml. of glycine solution were added to ensure complete co-ordination. The lanthanons were then fractionally precipitated from the solution at 80—90° by appropriate quantities of 10% aqueous oxalic acid. The final fraction was always formed slowly and required the addition of a few drops of ammonia solution to initiate precipitation. Individual fractions were filtered off, ignited to oxide, redissolved in acid, and their compositions determined, in some cases by spectrophotometric means, but in the majority of cases by visual, and spark, spectroscopy in comparison with standards, and absorptiometrically on the " Spekker " instrument. The results obtained are shown in Table I. Table Ia shows data obtained when insufficient complex was formed by the

<div align="center">TABLE I.</div>

<div align="center">*Co-ordination with glycine.*</div>

Fraction no.	La, %.	Pr, %.	Nd, %.	Sm, %.	Fractional wts.	Fraction no.	La, %.	Pr, %.	Nd, %.	Sm, %.	Fractional wts.
0	40	12·5	42·0	5·0	100	5	5	27	62	4	9
1	95	—	—	—	22	6	2	18	58	10	10
2	50	13	22	—	10	7	—	15	57	20	12
3	30	20	25	—	17	8	—	2	52	40	10
4	15	25	47	—	10						

<div align="center">TABLE Ia.</div>

<div align="center">*Partial co-ordination with glycine.*</div>

Fraction no.	La, %.	Pr, %.	Nd, %.	Sm, %.	Fraction no.	La, %.	Pr, %.	Nd, %.	Sm, %.
2	10	15	35	38	7	40	10	30	13
4	30	15	35	13	8	55	5	15	22

employment of excess of hydroxide. The reversal of the series is well shown; the values for samarium in the final fraction might be considered anomalous and due to the fact that the solution employed for spectrophotometry had a green tinge, possibly due to unknown impurities. On the other hand, it might be considered that with the partial removal of lanthanons from the system by precipitation, the liberated glycine sufficed to form complexes with all the residual earths, with the result that partial reversal of the fractionation was exhibited towards the tail of the series. The separation achieved in fully co-ordinated solution is reasonably good with respect to samarium and lanthanum; neodymium and praseodymium appear to split to a small degree but this effect is not noteworthy.

Octahedra from the faintly acid solution crystallise well, and the *lanthanum* complex was analysed [Found : La_2O_3, 45·0; $(NH_2 \cdot CH_2 \cdot CO_2)$, 61·1. $Ln(NH_2 \cdot CH_2 \cdot CO_2)_3$ requires La_2O_3, 45·2; $(NH_2 \cdot CH_2 \cdot CO_2)$, 61·5%].

Histidine Complexes.—Prepared similarly to the glycine complexes, those of the light earths, upon oxalate fractionation, yielded the results given in Table II.   A much better separation of samarium and lanthanum is obvious and a fair degree of neodymium/praseodymium separation is evident.

TABLE II.

Co-ordination with histidine.

Fraction no.	La, %.	Pr, %.	Nd, %.	Sm, %.	Fractional wts.	Fraction no.	La, %.	Pr, %.	Nd, %.	Sm, %.	Fractional wts.
0	40	12·5	42·0	5·0	100	4	2	15	80	3	16
1	95	—	—	—	25	5	—	8	67	10	15
2	45	18	28	—	20	6	—	4	50	50	8
3	25	35	56	2	16						

The initial lanthanon–histidine solution was quite clear (contrast the glycine complex) and yielded flat monoclinic crystals [Found : Ln_2O_3, 28·0 (average atomic weight of lanthanon 142) ; C, 36·1 ; N, 21·2. Calc. for $Ln(C_6H_8O_2N_3)_3$: Ln_2O_3, 27·5; C, 35·8; N, 20·9%].

Fractionation of a heavy lanthanon mixture of average atomic weight 115 did not yield very successful results.   Solution was easily obtained but oxalate fractionation, even when extended to 18 fractions, gave only a mediocre separation—the head fraction of average atomic weight 98, and the tail of 122. Visual spectroscopy showed erbium to be less in the first eight fractions than subsequently.

Complexes with Other Amino-acids.—Although not employed for separations, co-ordination compounds of lanthanon with cystine, glutamic acid, and aspartic acid were prepared in solutions containing a trace of chloride and crystallised until free from chloride.   The compound with cystine formed monoclinic rosettes [Found : Ln_2O_3, 33·0 ; S, 19·0 ; C, 21·0 ; N, 8·0.   Calc. for $Ln_2(C_6H_{10}O_4N_2S_2)_3$: Ln_2O_3, 32·8; S, 19·0 ; C, 21·4 ; N, 8·3%]; that with glutamic acid formed rhombic platelets [Found : Ln_2O_3, 46·6; C, 24·6; H, 3·05; N, 5·5.   Calc. for $Ln_2(C_5H_7O_4N)_3$: Ln_2O_3, 46·2; C, 25·0; H, 2·9; N, 5·85%]; and that with aspartic acid, monoclinic prisms [Found : Ln_2O_3, 49·6; C, 21·5; H, 2·0; N, 6·0. Calc. for $Ln_2(C_4H_5O_4N)_3$: Ln_2O_3, 49·0; C, 21·3; H, 2·2; N, 6·2%].

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