676. *Separation of the Lanthanons with the Aid of Ethylenediamine-NNN'N'-tetra-acetic Acid (" Enta " Acid). Part III.* The Salt $H_4Na_4Ln_4enta_5,24H_2O$ and its Use* (a) *in Fractional Crystallisation, and* (b) *in Double-sulphate Precipitation.*

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The easily prepared salt $H_4Na_4Ln_4enta_5,24H_2O$ gives a rapid separation of the lanthanons by fractional crystallisation. An equilibrium, such as $4Na[Ln\ enta],H_4enta \rightleftharpoons 3HLn\ enta + Na[Ln\ enta] + Na_3H\ enta$, with solid solution occurring, is believed to be the reason, HLn enta collecting in head crystals and Na[Ln enta] at the tail. Stability of $H_4Na_4Ln_4enta_5,24H_2O$ falls with decreasing basicity in the lanthanon series. The crystallisation is most effective for middle earths, but gives a rapid, rough concentration of the ytterbium earths. The potassium salt is isomorphous, but its use is not advantageous.

Small amounts of neodymium have been eliminated from $H_4Na_4Gd_4enta_5$ solution much more rapidly by double-sulphate precipitation than from gadolinium trichloride solution.

Two previous papers (*J.*, 1950, 1819; 1951, 1461 *) dealt with the use of ammonium enta as a solvent for lanthanon oxalates, and the crystallisation of a resulting complex, or the fractional reprecipitation of dissolved oxalate by addition of more oxalic acid, a mineral acid, or a simple lanthanon salt solution. Any other insoluble lanthanon salt taken into solution as a complex might prove an alternative to oxalate. The insoluble, normal enta salts, HLn enta, present a rather special case. The lanthanum and neodymium salts were prepared by Brintzinger, Thiele, and Muller (*Z. anorg. Chem.*, 1943, **251**, 285). The yttrium salt, $Y_4enta_3,24H_2O$, was found to be soluble (Brintzinger and Munkelt, *ibid.*, 1948, **256**, 65). All three were found to be simple salts.

(a) *Preparation of the Salt and its use in Fractional Crystallisation.*—The present work is concerned with the salt, $4Na[Ln\ enta],H_4enta,24H_2O$, which is easily prepared by boiling together lanthanon oxide, sodium hydroxide, and ethylenediaminetetra-acetic acid in the correct proportions. It is believed to be formed by all the lanthanons but is most stable in the cerium group. Possibly one or two members at the lutetium end do not form it. The isomorphous potassium salt has been prepared from a crude mixture, mainly of cerium and terbium earths. The potassium salt differs only very slightly from the sodium salt but it did not give as good a separation of the earths on fractionation. Even the sodium salt fractionation however is not as efficient as that with the double magnesium nitrate. In general character the salt is rather similar to the simple acetate tetrahydrate. Like the latter it does not melt when heated but appears to desiccate on the bottom of the vessel if heated with its mother liquor. Down the series from lanthanum to dysprosium any desiccated product readily dissolves in the hot solution, and no obvious change results short of actual charring. The earths early in the series soften to a glutinous mass, but gadolinium gives a hard cake. With erbium it appears that decomposition has taken place and a whitish, relatively insoluble, powder remains. This can however be taken up on addition of more water, but the solution then requires to be concentrated before $H_4Na_4Er_4enta_5,24H_2O$ can again be crystallised. The decomposition is only semipermanent; it can be avoided by adequate agitation. The observed facts are consistent with the view put forward later that the fifth enta acid group is held reversibly.

The first fractionation attempted was of the salt prepared from crude gadolinium oxide (300 g.). The material was opened up into nine fractions in six steps. The head fraction then showed no visible absorption bands through 10 cm. of hot concentrated solution. Fraction 2 showed a faint holmium band, which was stronger in fraction 3; these two fractions were faintly greenish with dysprosium. The bulk of the holmium was found in fractions 5 and 6, accompanied by a little erbium. Fraction 9 was poor in holmium but rich in erbium. A similar fractionation with some crude yttrium earths from yttriotungstite, much richer in coloured earths than the above gadolinium oxide, confirmed the rapidity of the separation of dysprosium, holmium, and erbium, and showed that thulium collected at the tail. These

* *J.*, 1950, 1819, and *J.*, 1951, 1461, are now considered to be Parts I and II of this series.

two series were later amalgamated and run with about 25 fractions; a good separation continued to be obtained. The process is more effective than bromate fractionation, but is more bulky, and lack of fusibility of the crystals causes difficulties. Mother-liquors require to be boiled separately from the solids, poured on to them, and then frequently shaken until solution has occurred. The solubility of the salt varies widely with temperature. In a sample of gadolinium it fell from 870 to 20 g. of salt per litre between boiling point and room temperature. The latter amount means that too little material passes down the series in the liquors. The room-temperature solubility of erbium is however considerably greater. Crystals up to 1 cm. diameter have been obtained but are more usually 1—4 mm. in diameter. They are smaller at the head of a series than at the tail, and are of irregular form. Present indications are that use of the salt might be preferred to bromates when only a small amount of material is to be handled, as for instance in the final purification of an element. The most suitable elements for treatment by this method appear to be those in the series from gadolinium to holmium, inclusive. The ease with which the salt can be prepared is a point in its favour. In the course of fractionation a definite acidity arises at the head and alkalinity at the tail. There is evidently a decomposition, and the formula assigned is no longer valid throughout the series. The very rapid initial separation is undoubtedly the result of this decomposition. The solubility, especially in cold solution, increases with complex stability, or $H_4Na_4Ln_4$ enta$_5$ instability. Thus the stronger bases collect in the acid head and the more stable complexes go to the tail. Naturally this separation of acid and base can only proceed to a limited extent. It has been found that at the head (Gd) a pH of about 5·5 (paper test) is the limiting value; at the tail gummy non-crystalline matter soon collects.

The salt has been prepared by three different methods and a 1 : 1 ratio of alkali to lanthanon observed. The amount of enta is generally 1·25 mols. per g.-atom of lanthanon, but it may be less in the yttrium group; in one experiment it appeared to be close to 1·20. Prepared synthetically from 4 mols. of sodium hydroxide, two of gadolinium oxide and five of the acid, the sole product after sufficient boiling was the salt conforming to the formula $H_4Na_4Gd_4$enta$_5$,24H_2O. By treatment of gadolinium oxide with enta acid and a limited quantity of water, dissolution of the oxide to a neutral solution took rather less acid than that required for the formation of HGd enta. There may therefore have been partial formation of Gd$_4$enta$_3$ corresponding to Brintzinger's yttrium salt. Treatment of this solution with 0·5 mol. of N-sodium hydroxide gave a partial precipitation of hydroxide which redissolved with 1 mol. Thus the salt in solution was initially, partly at least, simple but became complex. The solution at this point was strongly alkaline and the solute showed no ability to crystallise. Addition of enta acid to give a total of 1·25 mols. gave a neutral solution from which the solute crystallised well. The following series of reactions are suggested as the main course of the reaction :

$$2Gd_2O_3 \xrightarrow{4H_4enta} 4GdH\ enta \xrightarrow{4NaOH} 4Na[Gd\ enta] \xrightarrow{H_4enta} H_4Na_4Gd_4enta_5$$
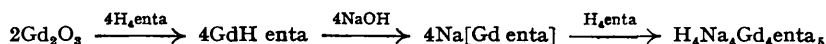
In the third method of preparation neutral gadolinium sulphate was treated with neutral trisodium enta. The reaction mixture became acid.

$$Gd_2(SO_4)_3 + 2Na_3H\ enta = 2Na[Gd\ enta] + 2Na_2SO_4 + H_2SO_4$$
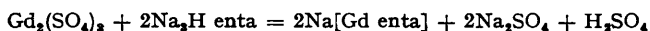
Gadolinium oxide was added to maintain neutrality. The complex gadolinium salt and the sodium sulphate were readily crystallised separately; the sodium sulphate exactly accounted for the sulphate originally combined with the gadolinium, but there was a shortage of one atom of sodium for each atom of gadolinium.

It was possible to prepare a soluble neodymium enta salt with at least partial success when neodymium oxide in excess was warmed with enta acid and a little water. The solution showed the characteristically sharpened absorption bands of anionic neodymium (Moeller and Brantley, *J. Amer. Chem. Soc.*, 1950, **72**, 5447). The salt is however unstable to heat, and Brintzinger *et al.* (*loc. cit.*) did not find it in hot dilute solution.

EXPERIMENTAL.

Crude gadolinium oxide from a monazite source was used for most of the synthetical work. It contained about 2% of neodymium oxide, a similar quantiy of dysprosium, and some terbium, but no samarium or europium.

Preparation of the Salt.—Gadolinium oxide (18·1 g., 0·05 mol.) and sodium hydroxide (4·0 g.) in boiling water (about 100 ml.) were treated with H$_4$enta till all the gadolinium was dissolved and a neutral solution obtained (Required 29 g., 0·125 mol.). The *salt* crystallised fairly completely on cooling, but by evaporation of the mother-liquor a further small crop was obtained; there was a very small quantity of a gummy material. The total yield was 58·8 g. (H$_4$Na$_4$Gd$_4$enta$_5$,24H_2O requires 58·3 g.).

In a second experiment, to gadolinium oxide (18·1 g.), moistened with a little water and warmed, enta acid was added till dissolution of the gadolinium oxide was complete [Consumed 22·3 g. of enta acid. GdH enta requires 23·6 g. (formation of some Gd_4enta_3 seems indicated)]. The gadolinium passed into solution after going through a glutinous stage. The solution readily formed a glutinous skin on the surface but no crystallisation was observed. To it was added N-sodium hydroxide (50 ml.); this caused some precipitation of hydroxide, but this redissolved when another 50 ml. of the alkali were added, indicating that the original solution contained some simple salt but that a sodium complex had now formed. The solution was now strongly alkaline. To it was added enta acid (6 g.). The pH was then 9; more acid (1 g.) reduced the pH to 3, and a good crop of salt crystallised.

When first encountered the salt was thought to be a sulphato-complex, but this was disproved by the following experiment.

Gadolinium sulphate octahydrate (187 g., 0·25 mol.) was treated with just sufficient M-solution of Na_3H enta (690 ml.) to bring about solution, the neutrality being maintained by addition of gadolinium oxide (13 g.). There was obtained the complex (316 g.), sodium sulphate decahydrate (156 g.), and, on addition of excess of hydrochloric acid to the mother-liquors, sodium chloride (31 g.). No free enta acid was precipitated [Found, corresponding to $Na_2SO_4 + NaCl$; SO_4, 71·7 g.; Na 34·4 g. Input: SO_4, 72 g.; Na, 47·5 g. This corresponds to an input to the complex: Na, 13·1 g.; Gd, 90·1 g.; H_4 enta, 161·8 g.; balance (water), 50·3 g. $H_4Gd_5Na_5enta_6,24H_2O$ requires Na, 13·1 g.; Gd, 89·7 g.; H_4 enta, 161·8 g.; H_2O, 49·4 g.]. This preparation formed about one-third of the material subsequently fractionated.

(b) *Double-sulphate Precipitation from Sodium Lanthanon Enta Solution.*—The solubility of lanthanon alkali sulphates follows the order of increasing complex stability, and the success of the usual process is itself undoubtedly the result of weak complex formation. If therefore a stronger complexing factor is introduced a sharper separation may be expected. The double-sulphate separation of a mixed earth has therefore been studied by both the normal procedure and starting with the complex salt, $H_4Na_4Ln_4enta_5$. The latter procedure gave a much sharper separation of the less soluble earths from the more soluble, but the more soluble salts proved difficult to precipitate at all. However, good recovery of the enta salt is possible because of its low solubility in cold acid solution, if no very heavy earths are present. Double-sulphate precipitation of lanthanon enta solutions is therefore useful chiefly as a means of cleaning small quantities of earths forming the less soluble double sulphates from larger quantities of material giving more soluble double sulphates. Thus it has proved valuable in removing a little neodymium from gadolinium which had been fractionated as double magnesium nitrates, but which, owing to the presence of yttrium, had not proved separable by this means.

For a mixture of earths containing neodymium oxide 2·4%, samarium oxide 13·2%, dysprosium oxide 10%, and much gadolinium a normal double-sulphate precipitation from 10% chloride solution was compared with precipitation from the complex enta solution. From the chloride solution the first 7% of earth to be precipitated contained 6·9% of neodymium oxide and the first 25% averaged 5·6%. Only 30% of the earth was recovered at the tail, free from neodymium. From enta solution the first 20% to be precipitated contained 9·1% of neodymium oxide, and the next 7% carried 1·7%, and left the solution quite free from neodymium.

Double-sulphate precipitation develops an excess of enta in solution, and further precipitation does not then take place. But by the addition of suitable simple lanthanon solution the excess of enta is utilised and further precipitation occurs. The precipitation is also facilitated by sulphuric acid. This will itself, in sufficient quantity, precipitate HLn enta in the cerium group. But if acidification is not carried to this point the salt existing in solution is precipitable more selectively as double sulphate.

$$H_4Na_4Ln_4enta_5 \xrightarrow{H_2SO_4} HLn\ enta \xrightarrow{Na_2SO_4} Ln_2(SO_4)_3,Na_2SO_4$$
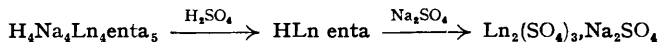
EXPERIMENTAL.

Crude gadolinium oxide (25 g.) in solution (300 ml.) as $H_4Na_4Gd_4enta_5$ was treated at the boiling point with sodium sulphate (15 g.), and boiling continued for 30 minutes. The precipitate was collected and more sodium sulphate (15 g.) added as before, without result. Sulphuric acid (2 ml.) was then added; a small precipitate resulted which carried down all the neodymium remaining in solution. Further precipitation on the addition of more acid was unsatisfactory, giving mixed double sulphate and enta salt.

The material used for the fractionation in (a) was dissolved in water (4 l.) and sodium sulphate (150 g.) added, and the solution acidified and boiled; a precipitate formed and was collected. No further precipitate formed on boiling the mother-liquors so a solution of an earth chloride mixture was added, having a neodymium content similar to the present content of the reaction mixture. Further precipitation now occurred. The process was repeated by using another chloride solution almost free from neodymium. There thus resulted three nearly equal fractions (43 g. of oxide) having, respectively, 10·3, 5·0, and 1·8% of neodymium oxide. The solution was then quite free from neodymium, and on storage deposited a crystalline complex (750 g.), leaving only a trace of erbium in solution. Previous

work had shown that while the neodymium collected in the head after ten series of crystallisations on ten fractions of the enta$_5$ salt the removal of the last traces of neodymium by this process would not prove outstandingly effective.

Sometimes double-sulphate precipitation occurred suddenly in an almost colloidal form and showing little selectivity. Such a precipitate redissolved when the solution was made more alkaline and was re-formed with satisfactory results by careful acidification.

The action of a little enta on double-sulphate precipitation was also studied. Sufficient Na$_3$H enta was added to crude terbium-earth chlorides to give about 25% complex formation. Practically no improvement in the elimination of neodymium or samarium occurred at the start, or indeed before about 75% of the earths had been precipitated, and enta was therefore present in full equivalent. Neodymium was by this time eliminated but samarium separation showed a distinct improvement (1·2% in solid at 85% precipitation as against 4% at 90% precipitation). The concentration of holmium and erbium at the tail was observed to be much improved but the contents were only small and therefore difficult to estimate accurately. The concentration of dysprosium in the fraction, 75—100% precipitation, was improved, the maximum of 25% to 31%. The content in the fraction 45—75% precipitation decreased from an average of 10% to 5%. The practical utility of enta for improving the concentration of earths collecting at the soluble end of a double-sulphate series was not however convincingly demonstrated. The fractional crystallisation of the enta salt appears preferable.

DISCUSSION.

The number of lanthanon and alkali lanthanon enta salts appears to be large and ill-defined. Besides Brintzinger's normal simple salt, HLn enta, the present work has shown the existence of a soluble, unstable, and largely complex, salt for which the formula Ln[Ln enta]$_3$ is suggested corresponding to the supposed alkali complex Na[Ln enta]. Since each [Ln enta] group presents the possibility of *cis-trans* isomerism four isomers are possible of the former salt. The nature of the absorption spectrum makes this formula more likely than an alternative based on the chelate character of the >N·CH$_2$·CO$_2$H group in HLn enta. This would give rise to a salt Ln$_4$enta$_3$ with only one Ln held in complex combination.

A major point of interest is the extra molecule of H$_4$enta found in the salt H$_4$Na$_4$Ln$_4$enta$_5$, though it is a mistake to think of it as in any way supernumerary, for it must bind together four [Ln enta] anions. When simple HLn enta is treated with alkali and passes to Na[Ln enta] one electrovalent but two covalent bonds are formed :
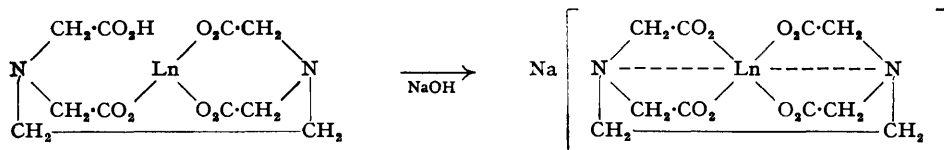
An elaborate system of five 5-membered rings comes into existence with hybridised bond orbitals. The result appears to be that the anion, after union with the sodium cation, has a residue of ammoniacal character and can co-ordinate with a hydrogen atom. The co-ordinated amine groups do not here behave as neutral groups as they do with elements which readily form amines. To maintain 6-co-ordination the lanthanon has to accept two amine groups, but the bond is weak and sufficient amine character is left to form a co-ordinate link with hydrogen. The more electropositive the lanthanon the greater is the stability of the enta$_5$ compound. Breakdown of this compound in aqueous solution is not likely to result in liberation of free enta acid but may take the course :

$$\text{Na[Ln enta],H}_4\text{enta} \rightleftharpoons 3\text{HLn enta} + \text{Na[Ln enta]} + \text{Na}_3\text{H enta}$$
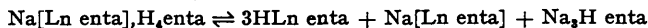
The phenomena already described appear to be satisfactorily accounted for on this hypothesis, if solid solution is easily formed between the various components of the system. HLn enta is only slightly soluble but Na[Ln enta] and Na$_3$H enta are highly soluble in water. If therefore a mixture of the above components but mainly enta$_5$ salt is crystallised the head crystals will be rich in HLn enta and the tail in Na[Ln enta]. At the same time a separation according to basic strength is brought about, the strong bases preferring the simple salt form and the weak bases the complex.

Fractionation by this process therefore depends upon instability of the 5-enta salt. In practice it has been found that the cerium earth salts are too stable to be worked satisfactorily. A concentration of the ytterbium earths in an uncrystallisable tail is rapidly obtained. The earths Gd, Tb, Dy, and Ho appear to be those which respond best to treatment.

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