Lanthanon Complexes with Hydrazine-NN-*diacetic Acid.*

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[Reprint Order No. 4159.]

A study has been made of the stable complexes formed between the lanthanons and hydrazinediacetic acid. Solid complexes have been prepared which exhibit a Ln : acid ratio of 1 : 3, and overall stability constants have been derived for some of the normal complexes formed; these range from 6·6 for the lanthanum complex to 7·7 for the ytterbium complexes. The yttrium complex has a stability constant value of 7·3. Spectrophotometric studies show the 576 mμ absorption band of the neodymium ion to exhibit, on formation of the hydrazinediacetate complex, the " internal " Stark effect splitting previously observed in absorption spectra of other complex neodymium ions.

The complexes formed are of little value in macroscale separation of the lanthanons.

HYDRAZINE-*NN*-DIACETIC ACID (" hda "), $NH_2{\cdot}N(CH_2{\cdot}CO_2H)_2$, was recently employed by Fitch and Russell (*Analyt. Chem.*, 1951, **23**, 1469) as eluant in the ion-exchange separation of lanthanum from the other lanthanons, but the information given was insufficient to enable correlation of the fundamental data for lanthanon–hda complexes with those for complexes between the lanthanons and ethylenediaminetetra-acetic acid (" enta ") and nitrilotriacetic acid (" trilo ") (Vickery, *J.*, 1951, 1817; 1952, 421, 1895). The work now recorded was undertaken to permit this correlation.

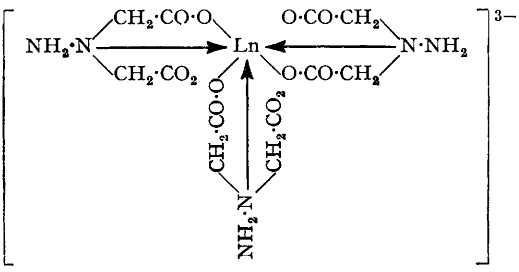
Fitch and Russell (*loc. cit.*) considered mono- and di-hda–lanthanon complex ions to be formed, but the acid–base titration curves given for the solutions employed showed no evidence of this. A series of titrations of Ln–hda in increasing molar ratios has now shown stable complexes to be formed only at a 1 : 3 molar ratio of Ln : acid (Fig. 1). The titration curves for the 1 : 2 and 1 : 3 ratios could indicate the formation of such salts as $Na[Nd\ hda_2]$ and $Nd[Nd_3\ hda_2]_3$, but (see p. 388) the first salt could not be prepared. The second salt would be insoluble (like the analogous enta complex), but, in fact, no precipitate was seen during or after the titrations.

p*K* values determined for hydrazinediacetic acid were : pK_1 2·54, pK_2 9·30, and these, with the evidence presented later, confirmed that hda acts monobasically towards the lanthanons. Since the 1 : 3 complexes must be formed stepwise (*e.g.*, Schwarzenbach, *Nature*, 1951, **167**, 434), the cationic mono- and di-acid complexes would exist transitorily through the reactions

$$\begin{aligned} Ln^{3+} + HA^- &\longrightarrow LnHA^{2+} \\ LnHA^{2+} + HA^- &\longrightarrow Ln(HA)_2{}^+ \\ Ln(HA)_2{}^+ + HA^- &\longrightarrow Ln(HA)_3 \end{aligned}$$

The formation of anionic species cannot be disregarded, however, and at pH values between 5·8 and 7·2 neodymium was extracted by anion-exchange resins from solutions of the complex. This evidence for anionic complex formation is supplemented by spectrophotometric data. Simple lanthanon salts with hydrazinediacetic acid can be prepared which also have a 1 : 3 molar ratio of lanthanon to acid, *i.e.*, $Ln(AH_2)_3$, but these exist only at pH values less than *ca.* 6·0. At this pH value, and below, the absorption spectra of the lanthanon salt solutions are characteristic of Ln^{3+} ions. With increase in pH of the solution the spectra change markedly and exhibit those variations which have been shown to occur on complex formation (Moeller and Brantley, *J. Amer. Chem. Soc.*, 1950, **72**, 5447; Tevebaugh, A.E.C.D. 2749; Vickery, *locc. cit.*). The absorption spectrum of neodymium complexes with hda presented analogies to those of the complexes with enta or trilo, but the internal Stark effect splitting of the 576 mμ band becomes marked only at alkaline pH values (Fig. 2). Differentiation from the spectrum of ionic solutions is slight below pH 6·0, but thereafter a progressive diminution in absorption intensity takes place together with a slight bathochromic shift of the 522 mμ band. At pH 8·2 splitting of the 576 mμ band is quite clear. Whether the peaks at 586 and 591 mμ are new bands or developments of the 576 mμ band is uncertain ; there is slight evidence of their existence at pH 6·2, but at pH 2·0 their presence is doubtful.

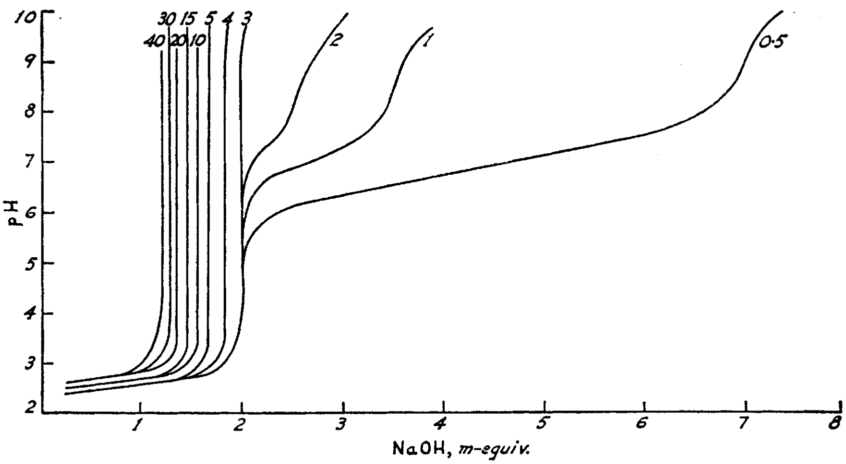
From the evidence available, the complexes formed in solution may be visualised as analogous to those with enta and trilo, and of the form (I), which includes three five-membered chelate rings.



(I)

By acidifying a neodymium chloride–ammonium hydrazinediacetate solution a compound was obtained whose analysis corresponded with $Nd[NH_2\cdot N(CH_2\cdot CO_2)_2H]_3,7H_2O$; this dissolved readily in water or aqueous ammonia but could not be recrystallised from the latter. Acid solutions of pH 6·0 did not dissolve the compound. Attempts to prepare complex sodium salts similar to those of enta and suitable for fractional crystallisation (Marsh, *J.*, 1951, 3057) were unsuccessful.

FIG. 1. *Titration of* $NdCl_3$–hda *solution against* NaOH.



The figures on each curve represent moles of hda per mol. of $NdCl_3$ in 100 ml. of solution containing 1×10^{-4} mol. of hda. For clarity, the curves for ratios 5—40 have been drawn semidiagrammatically.

With knowledge of the type of complex formed, the overall stability constants could be determined. Chelation occurring stepwise, the individual step equilibrium constants are :

$$K_1 = \frac{[LnHA^{2+}]}{[Ln^{3+}][HA^-]}; \quad K_2 = \frac{[Ln(HA)_2{}^+]}{[LnHA^{2+}][HA^-]}; \quad K_3 = \frac{[Ln(HA)_3]}{[Ln(HA)_2{}^+][HA^-]}$$

The integration of these step equilibria was affected as before (Vickery, *locc. cit.* ; Mellor and Maley, *Australian J. Sci. Res.*, 1949, **2**, 579), the values of K_1, K_2, and K_3 being those of pA at $n = 0{\cdot}5$, $1{\cdot}5$, and $2{\cdot}5$.

The acid–base titration curves and formation curves and the data obtained from them are given in Figs. 3 and 4 and Table 1. The overall stability constants (log K values) for hda do not completely confirm Fitch and Russell's observation (*loc. cit.*) that an appreciable difference exists in the degree of complex formation attained by lanthanum as compared with the other lanthanons. Even ytterbium, however, forming the strongest complexes of those examined, still is less strongly complexed with hda than is lanthanum

TABLE 1.

	hda					hda			
Lanthanon	log K_1	log K_2	log K_3	log K	Lanthanon	log K_1	log K_2	log K_3	log K
Lanthanum	3·8	2·8	$<0·1$	6·6	Yttrium	4·1	3·1	0·1	7·3
Samarium ...	4·1	2·9	0·1	7·1	Ytterbium ...	4·5	3·2	$<0·1$	7·7

with enta or trilo. The general increase in log K values with atomic number of the lanthanons is in conformity with other lanthanon complex series. The step constants, K_1, K_2, and K_3, show quite readily that the first two ligand bonds are stronger than the last.

FIG. 2. *Absorption spectra of* 0·1M-NdCl$_3$ + 0·5M-hda.

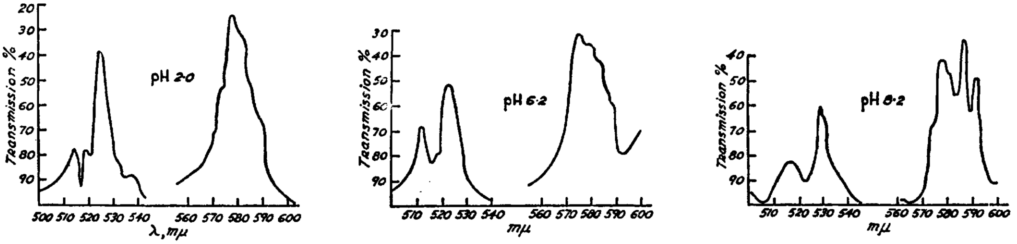


FIG. 3. *Titration of* Ln–hda *against* NaOH.

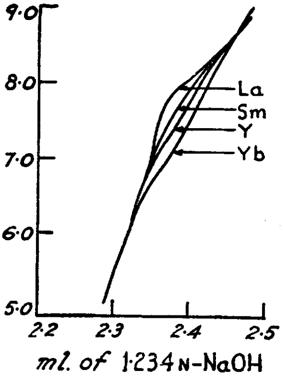
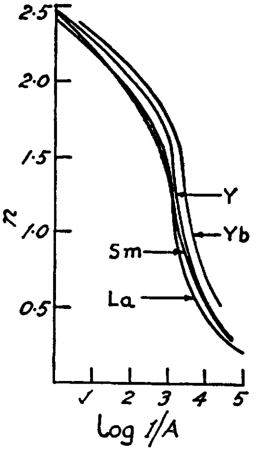


FIG. 4. *Formation curves for* Ln–hda *systems.*



The relatively low stabilities of these complexes explain why, unlike enta or trilo, hda does not readily sequester lanthanon oxalates. Much oxalate always remains undissolved when lanthanon oxalates are digested with ammoniacal hda solutions. The influence of pH on oxalate sequestration was demonstrated by shaking, for 14 hr. at room temperature, 10-g. lots of mixed lanthanon oxalates with solutions of 40-g. lots of ammonium hydrazinediacetate at pH values from 6 to 10. In spite of the excess of hda, solution was in no instance complete although the amount of residual oxalate decreased somewhat with increase in pH. Heating the solutions produced no further solvent effect. The possibility was at first considered that there might occur a preferential dissolution of lanthanon oxalates other than lanthanum (cf. Fitch and Russell, *loc. cit.*) but analyses of the dissolved and residual oxalates showed negligible variation in composition.

The sequestered oxalate solution showed little effective separation when fractionally acidified (Table 2). Fractions 1—3 were precipitated by addition of nitric acid, and fractions 4—6 by more oxalic acid, since the addition of nitric acid had ceased to yield a precipitate. Fractional oxalate precipitation from a lanthanon nitrate solution containing excess of ammonium hydrazinediacetate at pH 5·0 showed no better separation than before. Similar attempts to separate heavy lanthanon mixtures were unsuccessful.

TABLE 2.

	Pr_2O_3, %	Nd_2O_3, %	Sm_2O_3, %
Original	2·9	14·0	11·7
Fraction 1	1·8	8·6	5·5
„ 2	1·4	3·7	4·8
„ 3	1·5	8·7	4·1
Fraction 4	1·8	7·5	7·0
„ 5	4·1	23·7	12·8
„ 6	2·9	18·9	15·2

The sequestered oxalate solutions, however, yielded two polymorphic crystal forms: type α, deposited on cooling a hot, filtered solution of lanthanon oxalates in ammoniacal hydrazinediacetate; and type β, obtained on spontaneous evaporation of a cold prepared solution of the oxalates. Analyses of these crystals gave identical results, *viz.*, C, 24·1, 24·0; N, 13·9, 14·1; O, 42·8, 42·8; H, 3·5, 3·5; Ln, 15·7, 15·8; NH_4, 59·6, 59·5%. That the solutions were alkaline and retained lanthanon in solution is indicative of co-ordination. Ammonia was evolved on digestion with caustic alkali, but no lanthanon was precipitated, so we may consider the lanthanon to be present in the inner, and ammonium in the outer, Werner co-ordination spheres.

The α-type crystals were hexagonal with a high degree of twinning. The β-crystals were much smaller and acicular. The α-crystals were sparingly soluble in water, acids, and ammonia solution, but the β-crystals were quite soluble in all three reagents. The behaviour of these polymorphs is comparable with that of polymorphic glycine complexes previously described (Vickery, *J.*, 1950, 2058).

As well as these oxalato-complexes, another compound was prepared by acidifying a neodymium chloride–ammonium hydrazinediacetate solution. Analysis of this salt corresponded with $Nd[NH_2{\cdot}N(CH_2{\cdot}CO_2)_2H]_3,7H_2O$. This compound dissolved readily in water and ammonia solution but not in acid. Attempts to prepare complex sodium salt similar to those of "enta" suitable for recrystallisation (Marsh, *J.*, 1951, 3057) were unsuccessful.

EXPERIMENTAL

The hydrazinediacetic acid, prepared by the action of potassium chloroacetate on hydrazine hydrate (Bailey and Read, *J. Amer. Chem. Soc.*, 1914, **36**, 1747), was recrystallised, and its composition checked by analysis. According to Curtius and Hussong (*J. pr. Chem.*, 1861, **83**, 271), hda melts with decomposition at 166—167°. Bailey and Read (*loc. cit.*) found a somewhat higher decomposition temperature (176°) but the present work has confirmed the earlier figure. One or two preparations which showed a pinkish colour tended to decompose at temperatures above 167° but when they were recrystallised to a pure white material the m. p. 166° (decomp.) was constantly obtained. The solubility in water of hda at 26° was found to be 2·8 g./l., and at 100° 36·8 g./l. Dissociation constants were determined by the usual potentiometric methods.

The individual lanthanons employed for spectrophotometric and titration studies were of high purity, as has previously been noted (*J.*, 1952, 421). The hda showed negligible background absorption between 5 and 600 mμ (the region examined), and the spectrophotometric data were obtained on a Beckman DU instrument with the reading intervals, etc., as previously described. Titrations for the determination of stability constants were carried out at 25° with 1·23N-sodium hydroxide against 100 ml. of solution 1×10^{-3}M with respect to hda, $0{\cdot}2 \times 10^{-5}$M to Ln^{3+}, and 2×10^{-3}N to perchloric acid, the ionic concentration of the system being maintained at 0·1M by addition of potassium chloride. pH determinations were made on a Cambridge pH meter and taken as direct measurements of hydrogen-ion concentrations. Activity coefficients were neglected, as early determinations showed that their consideration led to little variation in the formation curve functions.

The lanthanon oxide (oxalate) mixtures employed for separation studies were derived from monazite (less cerium) or davidite (less much yttrium).

Thanks are due to Dr. Zimmermann of the Microanalytical Section of this organisation for microanalyses of the acids and complex salts prepared.

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[*Received, March* 11*th*, 1953.]