81. *Lanthanon Complexes with Ethylenediaminetetra-acetic Acid. Part II.**

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Complexes of the ammonium salt of ethylenediamine-*NNN'N'*-tetra-acetic acid with some members of the lanthanon series have been studied spectrophotometrically. Earlier work on these complexes has been extended, and the " internal " Stark effect splitting of the absorption spectra is shown to occur only with neodymium and erbium. Consideration is given to the suggestion that this phenomenon is due to a perturbation of the lanthanon ionic field, and this hypothesis is recast on the basis of lanthanon paramagnetism. Spectrophotometric data on the neodymium nitrilotriacetic acid complex are also presented.

THE value of complex formation in the separation of the lanthanons has recently been emphasised by Marsh (*J.*, 1950, 1879; 1951, 1461), studying the use of ethylenediamine-*NNN'N'*-tetra-acetic acid—" enta "—as its ammonium salt, in lanthanon separation. He paid particular attention to the use of ammonium enta in improved fractionations of mixtures of the heavy earths, whereas the author (Part I*) has studied its value in separation of the light lanthanons.

Moeller and Brantley (Illinois Univ. N60R1-71, Chem. Task VII, Sept. 1949; *J. Amer. Chem. Soc.*, 1950, **72**, 5447) studied the ammonium enta complexes of neodymium with particular reference to absorption spectra. Titration and ionic migration studies were also carried out to confirm conclusions drawn from the spectrophotometric data. The existence of a complex of 1 : 1 molar ratio of neodymium chloride and ammonium enta was postulated, and this has been confirmed by the preparative work of Marsh and of the author (*loc. cit.*). The possible existence of a further complex was discussed by Moeller and Brantley but the evidence for this was not considered conclusive; such data as were available related to complexes of different composition rather than the isomeric type for which evidence has been presented by the author (*loc. cit.*). Spectrophotometric studies on the neodymium complex carried out by Moeller and Brantley showed splitting of the main spectral absorption bands together with a shift of the bands towards longer wavelengths. This was ascribed to " an increase in the potential imposed on the system by the static symmetrical coulombic fields of the surrounding negative anions—the ' holohedric ' field potential "—which in turn was considered to indicate an increasing stability of structure. Tevebaugh (A.E.C.D. 2749; Declass., Nov. 1949) had similarly observed this " internal " Stark effect splitting in the absorption spectrum of citrate complexes of neodymium but considered the bands to be new entities and not derived from existing bands. This worker, moreover, observed band splitting only at comparatively high pH values, whereas it is known that the lanthanons and enta can form complexes at pH values in the region of 3·5—4·5.

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* Part I, *J.*, 1951, 1817.

Glueckauf and McKay (*Nature*, 1950, **165**, 594) considered some aspects of complex formation in the actinon series to indicate possible *f*-shell covalency. By analogy, similar bonding might be expected in the lanthanon series, and this would be demonstrated by variation in absorption spectra. It might therefore be considered that the strong complexes formed between the lanthanons and citrate or enta ions may well involve electrons in the 4*f* shell. This would be in accord with the known increase in stability of the lanthanon complexes with increasing atomic number and filling of the 4*f* shell, but would not account for the formation of a yttrium complex (having no 4*f* electron) with a stability intermediate between those of the gadolinium and dysprosium complexes (Marsh; Vickery; *locc. cit.*).

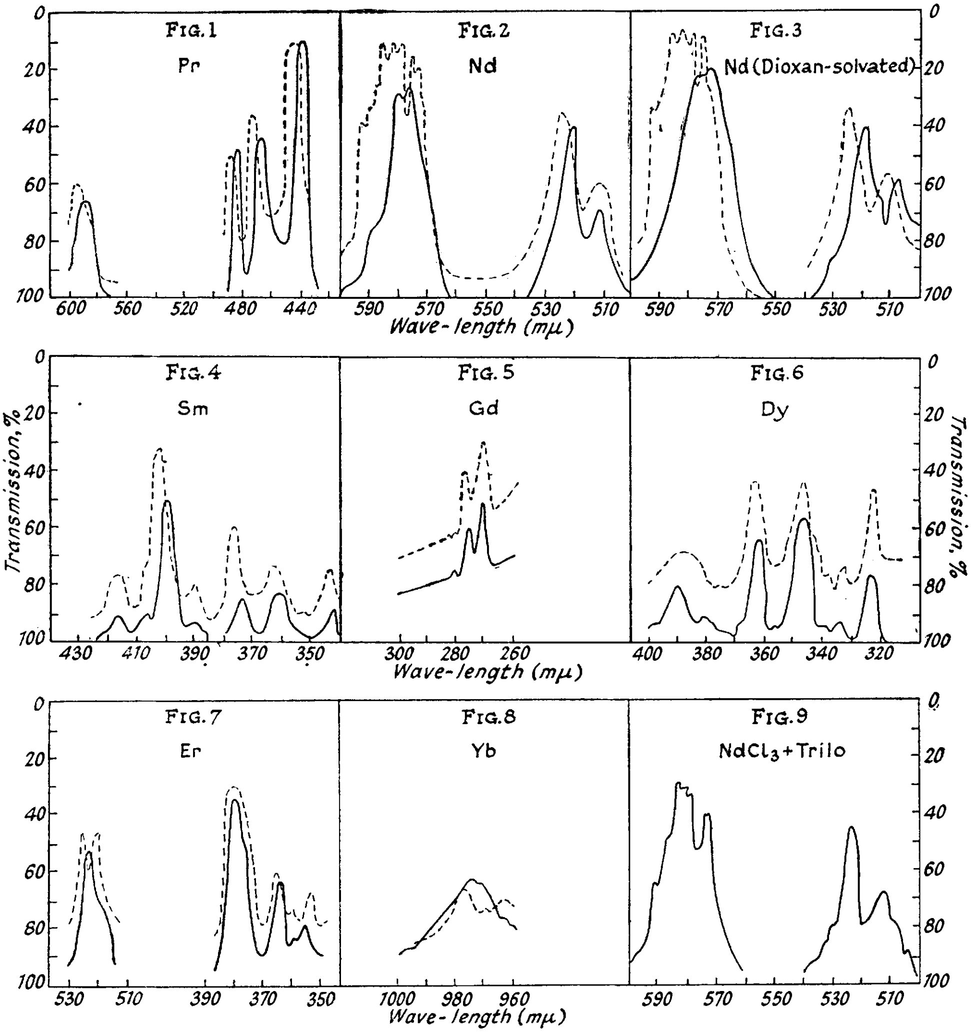
Separations of the lanthanons with enta, carried out by Marsh (*loc. cit.*), and titration studies by the author (*loc. cit.*, and in preparation), show that the stability of lanthanon–enta complexes increases with atomic number, so that if, as Moeller and Brantley (*loc. cit.*) affirm, splitting of absorption spectra is concurrent with stability, then, on proceeding through the lanthanon series, splitting of spectral absorption bands on complex formation should become increasingly multiple. It is now shown that this premise is not confirmed.

Alternatively, an increased shift of absorption bands towards longer wave-lengths might be expected with increasing stability; this has not been observed, but it must be remembered that Selwood (*J. Amer. Chem. Soc.*, 1930, **52**, 4308), in studying electron-shell deformation in concentrated solutions, found shifts to longer wave-lengths only in the light earths: europium and gadolinium absorption bands showed little movement, but those of holmium and erbium shifted towards the blue. Plumb, Martell, and Bersworth (*J. Phys. Coll. Chem.*, 1950, **54**, 1208) in spectrophotometric studies of various metal–enta complexes interpreted spectral displacements to the ultra-violet as due to complex formation, and Ephraim and Bloche (*Ber.*, 1926, **59**, 2692) considered shifts of absorption bands to the violet end of the spectrum to indicate compression of the 4*f* electron shell, and in studying lanthanon ammoniates found such a displacement to be at its maximum with praseodymium. Absorption shifts to higher wave-lengths on complex formation were attributed by Brode ("Chemical Spectroscopy," New York, 1939) to direct connexion of the additive group with the nucleus and formation of part of the chromophore; this would indicate a greater degree of chromophoric linkage with increasing shifts in absorption bands to lower frequencies. In the lanthanon series, however, the lighter, less firmly complexed elements show the greatest band shift towards lower frequencies. Brode's assertions cannot therefore be wholly tenable in this case; instead, there appears to be more correlation with the work of Selwood and of Ephraim and Bloche (*locc. cit.*) in that complexing initially distorts the electron shells by virtue of the potential of the surrounding anions, and that this is demonstrated by band displacement.

It is now apparent that, as the ionic radii of the lanthanons decrease with progression through the series, it becomes increasingly difficult for deformation of the electron shell to take place whilst at the same time the increase in electron density exerts an increasing binding effect on the electrons donated from the complexing agent. This would account for yttrium's taking up a position with lanthanons of similar ionic size, for the increase in stability of the complexes with atomic number, and for the collection together of the Sm–Eu–Gd triad.

Figs. 1—8 give data obtained with the Beckman spectrophotometer for 0·1M-solutions of lanthanon salts with and without the presence of 0·1M-ammonium enta. The shift of absorption to higher wave-lengths is seen to decrease with passage through the series, in conformity with Selwood's work (*loc. cit.*). Comparison of, *e.g.*, neodymium and erbium spectra at 510—530 mμ demonstrates that this band-shift is not merely a function of wave-length. Visual examination with a Hilger Barfit constant-deviation spectrometer indicated that shifts at band heads were always greater than at the tails so that, as well as the splitting in neodymium and erbium spectra, there is a tendency for overall widening of the band. The light earths were examined with chloride as the anion, and the heavy earths with perchlorate (Moeller and Brantley, *loc. cit.*; *Analyt. Chem.*, 1950, **22**, 433). Data obtained with the Beckman spectrophotometer showed band splitting to be detectable only in neodymium at the 576 mμ band and in erbium at the 523 mμ band. The expansion of the dysprosium 388 mμ band with enta (Fig. 6) is possibly due to impurities of holmium and/or erbium but is further discussed below. The ytterbium spectrum is peculiar and might be anomalous, but was nevertheless consistently obtained with the solutions employed. In all cases except that of ytterbium, complexing with ammonium enta decreased the transmission at band heads.

Absorption spectra of lanthanons complexed with ethylenediaminetetra-acetic acid (1–8) and nitrolotriacetic acid (9).



Full lines ——— *indicate normal absorption in* 0·1M-*solution.*
Broken lines – – – – *indicate absorption in* 0·1M-*complexed solution.*
Chloride is the anion in 1–5 and 9, perchlorate is the anion in 6–8.

The splitting of the 576 mμ band of neodymium into four peaks (Moeller and Brantley, *loc. cit.*) was confirmed spectrophotometrically, but not that of the 522 mμ band although the band shift was present. The American workers made spectrophotometric readings at 20 Å band widths through the ultra-violet to 600 mμ and at 50 Å from 600 to 1000 mμ with smaller intervals at absorption band heads. In obtaining the data presented here, readings were in 15—20 Å band widths, with 10 Å widths between 10 mμ on each side of peaks. It is thus difficult to appreciate why 522 mμ band splittings were not observed spectrophotometrically whilst that of the 576 mμ band was found. Visual spectroscopy showed no differentiation in the 522 mμ band.

It has been shown by Maley and Mellor (*Australian J. Sci. Res.*, 1949, *A*, **2**, 92) that the stabilities of chelated compounds are increased by the use of non-aqueous solvents. It was expected therefore that the partial replacement of solvent water by dioxan might invoke additional movement and splitting in absorption spectra. That this is so with neodymium is readily observed. The increased shift in dioxan solutions is obviously a solvent effect, whilst the higher degree of splitting observed is to be correlated with the fact that dioxan has only about one-fifth of the electrical moment of water.

As previously noted, optical examination of 4-cm. depth of enta-complexed solutions in the Hilger Barfit wave-length spectrometer gave no indication of splitting of the 522 mμ band of neodymium, but showed well the splitting of the 576 mμ band. No splitting of praseodymium and samarium absorption bands could be detected with the Beckman instrument, the Hilger-Barfit spectrometer, or the larger Littrow instrument.

The occurrence of detectable band splitting in only neodymium and erbium spectra among the lanthanons examined introduces interesting considerations. If we accept Moeller and Brantley's postulate that variations in band height and wave-length are attributable to increased potential (both hemihedric and holohedric) on the lanthanon ionic field, and that this also influences splitting of absorption bands, we have to explain the occurrence of this splitting only in neodymium and erbium spectra. Even if splitting of the absorption bands of other elements should be observed with instruments capable of higher resolution, it must still be determined why neodymium and erbium should display the strongest degree of band splitting. Neodymium and erbium, containing respectively three and eleven 4*f* electrons, may be considered the central members of their respective sub-groups in the lanthanon series. It is recognised that 0, 7, and 14 electrons in the 4*f* shell bestow a certain degree of stability upon the lanthanon configuration, and it is significant that neodymium and erbium, whose absorption spectra exhibit the greatest "internal" Stark effect, are the lanthanons most removed from these stable configurations. The apparent anomaly in the dysprosium 388 mμ band may well be viewed in this light as attributable to a Stark-effect splitting incompletely mature, even at the high position of this element on the magnetic susceptibility curve, owing to a residual tendency for dysprosium to revert to the stable gadolinium structure. In this respect studies on holmium and thulium absorption spectra might prove useful.

In studies of copper and nickel complexes, Russell, Cooper, and Vosburg (*J. Amer. Chem. Soc.*, 1943, **65**, 1301, 2329) found a linear relationship to exist between the magnetic moments and the maximum frequencies of light absorption. This would approximately correlate the splitting of neodymium and erbium spectra with the location of these two elements in the magnetic susceptibility curves for the lanthanons; but neodymium and erbium do not represent maxima in these curves as they do in absorption spectra: however, with the tendency of the absorption bands to shift to higher wave-lengths on complex formation, there might also exist a tendency for the magnetic-moment curves to shift to one side throughout the series on complex formation. Russell *et al.* showed that the magnetic susceptibilities of Ni^{2+} and Cu^{2+} decreased on complex formation, and it might well be, in the lanthanon series, that the susceptibilities similarly decrease where there is a tendency for the lanthanon ion to approach a stable configuration.

This premise has yet to be studied, but should its validity be shown, it would indicate an addendum to the suggestions of Van Vleck ("Theory of Electric and Magnetic Susceptibilities," Oxford Univ. Press, 1932) and Pauling ("The Nature of the Chemical Bond," Cornell Univ. Press, 1942) that, when the formation of a bond with a paramagnetic ion is accompanied by a small reduction in magnetic moment, it is the orbital contribution to the moment that is reduced. If therefore the internal Stark effect inducing the absorption-band splitting be attributable to an increase in the orbital contribution, it may thus indicate the possibility of hybrid bonding utilising the 4*f* electron level.

Similar to the use of enta in lanthanon fractionation was the earlier use by Beck (*Helv. Chim. Acta*, 1946, **29**, 357; *Mikrochem.*, 1947, **33**, 344; *Anal. Chim. Acta*, 1949, **3**, 41) of "trilo" (nitrilotriacetic acid ammonium salt). Although trilo cannot compete with enta for efficiency of separation of the lanthanons, it was thought that a comparison of the absorption spectrum of the neodymium ion and of its complexes with trilo and enta (Fig. 2) would be of interest. It was not possible to obtain data for the complex in a water–dioxan system owing to the immiscibility of the water-solvated complex with dioxan, but Fig. 9 shows the absorption of the 0·1M-neodymium–trilo complex in water. Measurements were made as before, and again splitting and displacement of the 576 mμ band are apparent but not of the 522 mμ band. Intensity does not develop to the same extent as with the enta complexed ion owing to the smaller molecular size of trilo than of enta, but the "internal" Stark effect is nevertheless apparent. The band shift for the 576 mμ band in trilo is much greater than for enta, but there is negligible difference in the 522 mμ band shifts.

EXPERIMENTAL

The lanthanon oxides employed were of the following purities: lanthanum, >99·8; praseodymium, >99; neodymium, "Specpure;" samarium, >99·5; gadolinium, *ca.* 96; dysprosium, *ca.* 96; erbium, >96; ytterbium, *ca.* 99; yttrium, >99·8%; all other general reagents were of analytical quality. Enta had originally been derived from two sources: one, a sub-analytical grade, and the other, designated "Sequestrene AA" by the Alrose Chemical Co., U.S.A., much purer. Moeller and Brantley (*loc. cit.*) examined the absorption spectrum of the latter material and found no absorption in the visible and only background absorption in the ultra-violet from 270 to 210 mμ. In the Sequestrene used in this work transmission was of the order of 98% throughout the region examined. The sub-standard material employed for general separations showed transmission of 96·5—97·5% from 1000 to 400 mμ, decreasing then to 70% at 325 mμ. It is evident that care must be taken in the selection of enta supplies for spectrophotometric work: in the transmission values reported here corrections for adventitious absorption were made by utilising 0·1M-enta as the standard in the Beckman instrument. A noteworthy point is the solubility in water of the enta employed by Moeller and Brantley, who quote this as being "about 1%." Sequestrene AA is stated by the suppliers to be 0·03% soluble in water: this has been confirmed for the material employed in this work.

Absorption-spectrum studies were made on a Beckman DU quartz prism spectrophotometer.

0·2M-Solutions of the lighter lanthanons were prepared by dissolving the appropriate weight of oxide in hydrochloric acid, evaporating to dryness twice to remove excess of acid, and redissolving in water to 100 ml. volume. For the heavy earths, perchloric acid was used for dissolution, care being taken to use only just enough acid completely to dissolve the oxide with very little excess; the perchlorate solutions were used as prepared without intermediate evaporation to dryness.

0·2M-Ammonium enta was prepared by dissolving 7·84 g. of H_4 enta in dilute ammonia at 60°, boiling for 10 minutes to remove excess ammonia, cooling, and diluting to 100 ml. Absorption measurements were made on mixtures of 5-ml portions of lanthanon and enta solutions, so that the concentrations in the cell were 0·1M. for each component. Readings were standardised against 0·1M-enta. Absorption measurements of the uncomplexed lanthanons were made on 5 ml. of lanthanon solution plus 5 ml. of water, these readings being standardised against water.

When dioxan was to be introduced into the system, 10 ml. of 0·2M-lanthanon solution and 10 ml. of 0·2M-enta were mixed, evaporated to 10 ml., and diluted again to 20 ml. with redistilled dioxan. The solutions then examined were thus 0·1M with regard to both lanthanon and enta in 50% dioxan, and measurements were made against 0·1M-enta in 50% dioxan prepared in the same way with water replacing the lanthanon solution.

Spectrographic examinations were made through 4-cm. thickness of solutions prepared as above. The extent and accuracy of the spectrophotometric readings have been given above and the data obtained are shown in Figs. 1—8.

Data in the case of neodymium–trilo complex were similarly obtained and are shown in Fig. 9. 0·2M-Trilo was prepared by dissolving 4·06 g. of trilo in dilute ammonia, boiling off excess of base, cooling, and diluting the solution to 100 ml.

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