Metal Chelates of Lanthanoids in Aqueous Solution and their Analytical Applications

By S. P. Sangal

Abstract

A detailed study on the composition, stability and analytical applications of Rare Earth chelates with Aluminon, Chrome Azurol S, Thoron, Chromotrope 2B and Alizarin Red S have been described. The composition have been ascertained spectrophotometrically using the Method of Continuous Variations, Mole Ratio Method and the Slope Ratio Method. The range for adherence to Beer's law, sensitivity and other optimum conditions required in the analytical applications have been described.

The chemistry of the rare earth elements has fascinated the chemist ever since their discovery in 1794. The years that followed were devoted mainly to the identification of the individual rare earths and their separation. Rare earths have in recent years found applications in maser and laser equipments, for nuclear control rods and shielding in super conductors and in filters in spectroscopy. Recently the International Union of pure and applied chemistry (1) has adopted the name lanthanoids for elements No. 57—71 in place of the earlier terms lanthanides and lanthanons.

Particular interest is now being taken in the analytical chemistry of the lanthanoids which, in addition to separation methods include procedures for their detection and determination as well. For the determination of the lanthanoids the colorimetric method has been quite popular in which the use of chromogenic reagents are made and light absorption studies of the coloured chelates permit the determination of the element in question. Unfortunately, no specific reagent has yet been discovered for the individual lanthanoids, but the chromatography and ionexchange procedures enable a sharp separation of individual lanthanoids and hence the specificity of a reagent is perphas no longer quite so important in the final spectrophotometric determinations. The main requirements of such reagents are [1]) high sensitivity [2]), water solubility and [3]) reproducibility.

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[1]) I. U. P. A. C., Compt. Rend. XXII Conference, London, July 1963, London (1964).

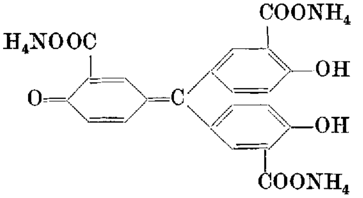
[2]) P. Job, Compt. Rend., **180**, 928 (1925); Ann. Chim. (X.) **9**, 113 (1928).

[3]) J. H. Yoe and A. L. Jones, Ind. Eng. Chem. Analyst. Ed. **16**, 111 (1944).

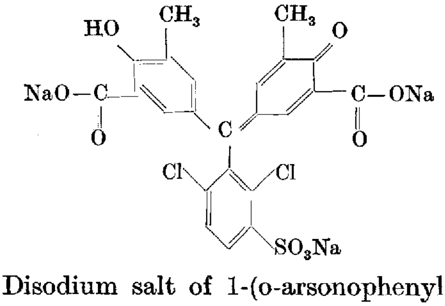
The chromogenic reactions involving a metal ion and a suitable polyfunctional donor (more often an organic compound) were noted long ago, but the use of these reactions in quantitative analysis were only possible with precision when instruments were designed to measure the intensity of colour accurately. The introduction of sensitive spectrophotometers about thirty years ago, gave a great impetus to the methodology and technique of photometric determinations. Inspite of the enormous amount of work on the applications of the coloured chelates in inorganic analysis sufficient attention has not been paid to the nature, composition and stabilities of the metal chelates formed with the metal ions and especially the lanthanoids.

The present work aims at a detailed investigation of a number of coloured metal chelates of the lanthanoids which have been described for the first time. The chelating ligands investigated here are organic dyes containing quinoid, phenolic and/or carboxylic oxygens as the donors. The ligands studied here are as follows:

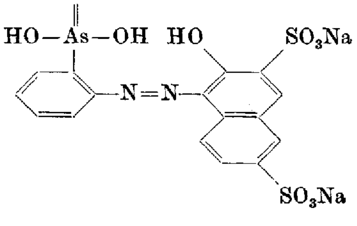
(1) Ammonium aurintricarboxylate (Aluminon)



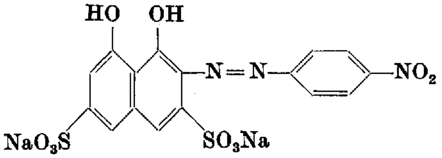
(2) Trisodium salt of 3″-sulpho-2″:6″-dichloro-3:3′-dimethyl-4-hydroxyfuchson-5:5′-dicarboxylic acid (Chrome Azurol S).



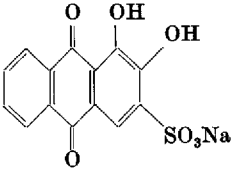
(3) Disodium salt of 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonic acid (Thoron)



(4) Disodium salt of p-nitrobenzene azochromotropic acid (Chromotrope 2 B)



(5) Sodium 1:2 dihydroxy anthraquinone-3-sulphonate (Alizarin Red S)



A number of methods are known for the determination of the composition of metal chelates in aqueous solutions using absorbance measurements, but in the present work only the following three methods have been employed.

1. The method of continuous variations (2).
2. The mole ratio method (3).
3. The slope ratio method (4).

The stability constant is useful for the understanding of the characteristics of a chelate (or a complex) but the determination of thermodynamic constants is beset with difficulties and it is often convenient and yet valuable to determine the stoichiometric constants, which describe the stability of species under a given set of experimental conditions. Hence in the present work for the determination of stoichiometric stability constants three different methods have been employed, viz., (a) the method of Dey et al.[5]) (b) the method of continuous variations using non equimolecular solutions and (c) the mole ratio method. From the values of stability constants the free energy changes of formation have also been calculated.

A detailed investigation of the metal chelates of trivalent praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium with ammonium aurintricarboxylate (Aluminon, abbr. AAC) have been described. The

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[4]) A. E. Harvey and D. L. Manning, J. Amer. chem. Soc. **72**, 4488 (1950); **74**, 4744 (1952).

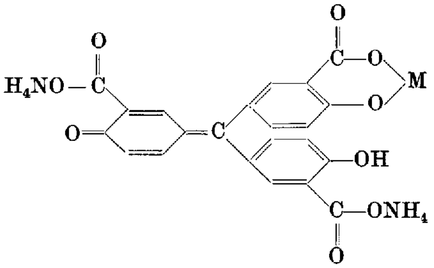
[5]) A. K. Mukherji and A. K. Dey, Analyt. Chim. Acta **18**, 324 (1958); J. Inorg. Nucl. Chem. **6**, 314 (1958).

results on the characteristics, composition of the metal chelates, stability constants as determined by three methods, and the analytical applications of AAC are summarized in the tables 1—3.

Table 1
Characteristics of AAC Chelates

Metal chelate	λ_{max} (mμ)	Composition M:Ke	pH range of stability
Pr (III)—AAC	540	1:1	4.5—8.5
Nd (III)—AAC	540	1:1	4.5—8.0
Sm (III)—AAC	540	1:1	4.5—8.5
Eu (III)—AAC	540	1:1	4.5—8.0
Gd (III)—AAC	540	1:1	4.5—8.0
Tb (III)—AAC	540	1:1	4.5—8.5
Dy (III)—AAC	540	1:1	4.5—8.0
Ho (III)—AAC	540	1:1	4.5—8.0
Er (III)—AAC	540	1:1	4.5—8.0
Tm (III)—AAC	540	1:1	4.5—8.0
Yb (III)—AAC	540	1:1	4.5—8.5
Lu (III)—AAC	540	1:1	4.5—8.5

The structure of the lanthanoid-AAC chelate is believed to be as follows:



The chelation occurs between the phenolic and adjacent carboxylic oxygens which has been ascertained on the basis of the liberation of hydrogen ions as a result of chelation.

The chelates of trivalent samarium, europium, gadolinium, terbium, dysprosium and holmium with trisodium salt of 3″-sulpho-2″:6″-dichloro 3:3′-dimethyl-4-hydroxyfuchson-5:5′-dicarboxylic acid (Chrome Azurol S, abbr. CAS) have also been described. The characteristics, composition, stability and analytical applications of CAS chelates described in the present work are summarized in tables 4—6.

Table 2
Stability Constants of AAC Chelates
pH 6.0, Temperature 25 °C

Metal chelate	log K	$\Delta G°$ K. Cals	Method
Pr (III)—AAC	4.2 ± 0.1	−5.8 ± 0.1	(a)
	4.3 ± 0.1	−5.9 ± 0.1	(b)
	4.4 ± 0.1	−6.0 ± 0.1	(c)
Nd (III)—AAC	4.4 ± 0.1	−6.1 ± 0.1	(a)
	4.4 ± 0.1	−6.1 ± 0.1	(b)
	4.4 ± 0.1	−6.1 ± 0.1	(c)
Sm (III)—AAC	4.5 ± 0.1	−6.2 ± 0.1	(a)
	4.5 ± 0.1	−6.2 ± 0.1	(b)
	4.5 ± 0.1	−6.2 ± 0.1	(c)
Eu (III)—AAC	4.6 ± 0.2	−6.3 ± 0.2	(a)
	4.5 ± 0.1	−6.2 ± 0.1	(b)
	4.6 ± 0.05	−6.3 ± 0.05	(c)
Gd (III)—AAC	4.8 ± 0.2	−6.6 ± 0.2	(a)
	4.6 ± 0.2	−6.3 ± 0.2	(b)
	4.6 ± 0.05	−6.3 ± 0.05	(c)
Tb (III)—AAC	4.8 ± 0.2	−6.6 ± 0.2	(a)
	4.7 ± 0.1	−6.4 ± 0.1	(b)
	4.6 ± 0.1	−6.3 ± 0.1	(c)
Dy (III)—AAC	4.9 ± 0.05	−6.8 ± 0.05	(a)
	4.9 ± 0.1	−6.8 ± 0.1	(b)
	4.7 ± 0.1	−6.4 ± 0.1	(c)
Ho (III)—AAC	5.0 ± 0.4	−6.9 ± 0.4	(a)
	4.9 ± 0.1	−6.8 ± 0.1	(b)
	4.9 ± 0.05	−6.7 ± 0.1	(c)
Er (III)—AAC	5.1 ± 0.2	−7.0 ± 0.2	(a)
	5.0 ± 0.2	−6.9 ± 0.2	(b)
	4.9 ± 0.1	−6.8 ± 0.1	(c)
Tm (III)—AAC	5.1 ± 0.1	−7.0 ± 0.2	(a)
	5.2 ± 0.1	−7.2 ± 0.1	(b)
	5.0 ± 0.05	−6.9 ± 0.05	(c)
Yb (III)—AAC	5.2 ± 0.2	−7.2 ± 0.1	(a)
	5.3 ± 0.05	−7.3 ± 0.05	(b)
	5.1 ± 0.05	−7.0 ± 0.2	(c)
Lu (III)—AAC	5.3 ± 0.4	−7.3 ± 0.4	(a)
	5.5 ± 0.2	−7.6 ± 0.2	(b)
	5.2 ± 0.2	−7.1 ± 0.2	(c)

Table 3
Analytical Applications of AAC Chelates
Wavelength of study 550 mμ; Temperature 25°; pH 6.0

Metal ion	Range for adherence to BEER's law p.p.m.	Sensitivity index (Sandell) γ^3cm^2
Pr (III)	0.37—15.9	0.056
Nd (III)	0.35—17.35	0.057
Sm (III)	0.40—18.0	0.058
Eu (III)	0.45—18.2	0.038
Gd (III)	0.42—18.8	0.039
Tb (III)	0.42—19.0	0.039
Dy (III)	0.43—19.4	0.040
Ho (III)	0.43—14.7	0.041
Er (III)	0.44—20.0	0.042
Tm (III)	0.54—24.3	0.042
Yb (III)	0.46—24.9	0.043
Lu (III)	0.46—25.2	0.043

Table 4
Characteristics of CAS Chelates

Metal chelate	λ_{max} (mμ)	Composition M:Ke	pH range of stability
Sm (III)—CAS	490	1:1	5.0—6.5
Eu (III)—CAS	540	1:1	4.5—8.5
Vd (III)—CAS	510	1:1	5.0—8.5
Tb (III)—CAS	500	1:1	4.5—8.0
Dy (III)—CAS	530	1:1	5.0—7.5
Ho (III)—CAS	550	1:1	5.5—8.5

A tentative structure of the CAS-lanthanoid chelates has also been suggested which is as follows:

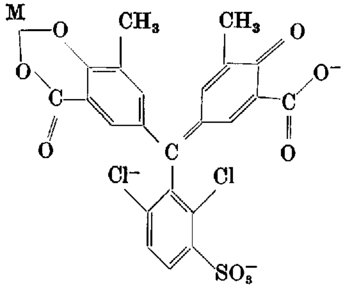


Table 5
Stability Constants of CAS Chelates
pH 6.0; Temperature 25°

Chelate	log K	ΔG° K. Cals	Method
Sm (III)–CAS	4.8 ± 0.2	−6.6 ± 0.2	(a)
	5.2 ± 0.2	−7.2 ± 0.2	(b)
	5.2 ± 0.1	−7.2 ± 0.1	(c)
Eu (III)–CAS	4.2 ± 0.1	−5.8 ± 0.1	(a)μ
	4.7 ± 0.1	−6.4 ± 0.2	(b)
	4.9 ± 0.2	−6.8 ± 0.2	(c)
Gd (III)–CAS	4.4 ± 0.2	−6.1 ± 0.3	(a)μ
	5.0 ± 0.1	−6.9 ± 0.1	(b)
	5.0 ± 0.2	−6.9 ± 0.2	(c)
Tb (III)–CAS	4.7 ± 0.2	−6.4 ± 0.3	(a)
	4.7 ± 0.1	−6.4 ± 0.2	(b)
	4.9 ± 0.2	−6.8 ± 0.2	(c)
Dy (III)–CAS	4.2 ± 0.1	−5.8 ± 0.1	(a)
	4.3 ± 0.1	−5.9 ± 0.1	(b)
	4.6 ± 0.1	−6.3 ± 0.2	(c)
Ho (III)–CAS	4.3 ± 0.2	−5.9 ± 0.2	(a)
	4.7 ± 0.2	−6.4 ± 0.3	(b)
	4.9 ± 0.2	−6.8 ± 0.2	(c)

Table 6
Analytical Applications of CAS Chelates
pH 6.0; Temperature 25°

Metal ions	Wavelength of study (mμ)	Adherence to Beer's law p.p.m.	Sensitivity index (Sandell) γ^3cm^2
Sm (III)	520	0.40–10.0	0.075
Eu (III)	550	0.33–10.9	0.056
Gd (III)	520	0.42–11.4	0.078
Tb (III)	520	0.42–11.4	0.053
Dy (III)	540	0.43–11.7	0.069
Ho (III)	550	0.44–11.9	0.082

The chelate is anionic as determined by the ion-exchange resin and electrophoretic studies. This is only possible if the chelation takes place between the hydroxyl and carboxylic oxygens and not between quinoid and carboxylic oxygens which would lead to the formation of a neutral complex.

The results on a detailed study of trivalent europium, terbium, ytterbium and lutecium chelates with sodium 1-(o-arsonophenylazo)-2-naphthol-3:6-disulphonate (Thoron; abbr. APANS) are summarized in tables 7—9.

Table 7
Characteristics of the APANS Chelates

Chelates	λ_{max} (mμ)	Composition M:Ke	pH range of stability
Eu (III)—APANS	500	1:2	3.5—7.5
Tb (III)—APANS	500	1:2	3.5—7.5
Yb (III)—APANS	500	1:2	3.5—8.0
Lu (III)—APANS	500	1:2	3.5—7.5

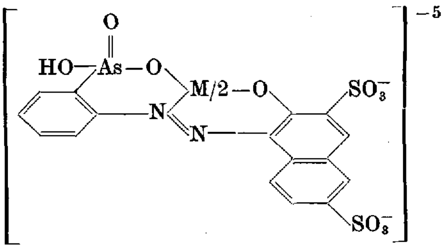
Table 8
Stability Constants of APANS Chelates
pH 4.0 ± 0.2; Temperature 25°

Chelate	log K	$\Delta G°$ K. Cals	Method
Eu (III)—APANS	8.2 ± 0.2	−11.3 ± 0.2	(a)
	8.6 ± 0.2	−11.9 ± 0.2	(b)
	8.4 ± 0.4	−11.6 ± 0.4	(c)
Tb (III)—APANS	8.9 ± 0.3	−12.3 ± 0.3	(a)
	8.7 ± 0.2	−12.0 ± 0.2	(b)
	8.8 ± 0.1	−12.2 ± 0.1	(c)
Yb (III)—APANS	9.6 ± 0.2	−13.3 ± 0.2	(a)
	9.7 ± 0.2	−13.4 ± 0.2	(b)
	9.3 ± 0.1	−12.9 ± 0.1	(c)
Lu (III)—APANS	9.7 ± 0.2	−13.4 ± 0.2	(a)
	9.7 ± 0.2	−13.4 ± 0.2	(b)
	9.5 ± 0.1	−13.1 ± 0.1	(c)

Table 9
Analytical Applications of APANS Chelates
pH 4.0; Temperature 25°

Metal ion	Wavelength of study (mμ)	Adherence to Beer's law p.p.m.	Sensitivity index (Sandell) γ/cm^2
Eu (III)	535	0.40—12.8	0.076
Tb (III)	545	0.42—14.3	0.071
Yb (III)	545	0.46—12.4	0.086
Lu (III)	545	0.46—12.5	0.087

A tentative structure of lanthanoid-APANS chelates may be suggested as follows:



The chelates have been found to be anionic as confirmed by the electrophoretic studies and also by the complete adsorption of the chelate by ion exchange resin Amberlite IR 45 (OH).

The metal chelates of trivalent europium, thulium, ytterbium and lutecium with disodium salt of p-nitrobenzene azochromotropic acid (Chromo-

Table 10
Characteristics of CTB Chelates

Chelate	λ_{max} (mμ)	Composition M:Ke	pH range of stability
Eu (III)—CTB	530	1:1	4.0—7.5
Tm (III)—CTB	540	1:1	5.0—7.5
Yb (III)—CTB	540	1:1	5.0—7.5
Lu (III)—CTB	540	1:1	5.0—7.5

Table 11
Stability Constants of CTB Chelates
pH 6.0; Temperature 25°

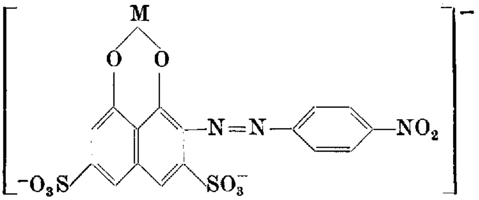
Chelate	log K	ΔG° K. Cals	Method
Eu (III)—CTB	4.7 ± 0.3	−6.5 ± 0.3	(a)
	5.0 ± 0.2	−6.9 ± 0.2	(b)
	4.95 ± 0.1	−6.85 ± 0.1	(c)
Tm (III)—CTB	5.0 ± 0.2	−6.9 ± 0.2	(a)
	5.0 ± 0.2	−6.9 ± 0.2	(b)
	5.25 ± 0.05	−7.2 ± 0.1	(c)
Yb (III)—CTB	4.3 ± 0.2	−5.9 ± 0.2	(a)
	5.2 ± 0.2	−7.2 ± 0.2	(b)
	5.3 ± 0.2	−7.3 ± 0.2	(c)
Lu (III)—CTB	5.2 ± 0.2	−7.2 ± 0.2	(a)
	5.6 ± 0.2	−6.4 ± 0.2	(b)
	5.3 ± 0.1	−7.3 ± 0.1	(c)

trope 2 B; abbr. CTB) have also been studied. The results on the characteristics, composition, stability and the analytical application of CTB are summarized in the tables 10—12.

Table 12
Analytical Applications of CTB Chelates
pH 6.0; Temperature 25°

Metal ion	Wavelength of study (mμ)	Range for adherence to Beer's law (p.p.m.)	Sensitivity (Sandell) γ/cm²
Eu (III)	580	0.40—18.0	0.08
Tm (III)	580	0.45—12.2	0.084
Yb (III)	580	0.46—15.6	0.086
Lu (III)	580	0.46—21.0	0.0875

The chelates have been found to be anionic in nature as determined by the electrophotetic and ion exchange resins. Hence the following structure of lanthanoid-CTB chelate may tentatively be suggested:



The chelates of sodium 1:2 dihydroxy anthraquinone-3-sulphonate (Alizarin Red S; abbr. ARS) with trivalent gadolinium, terbium, ytterbium and lutecium have been studied in detail. The results are summarized in tables 13—15.

Table 13
Characteristics of ARS Chelates

Chelate	λ_{max} (mμ)	Composition M:Ke	pH range of stability
Gd (III)—ARS	520	1:2	4.5—7.5
Tb (III)—ARS	530	1:2	3.5—7.0
Yb (III)—ARS	530	1:2	3.5—7.5
Lu (III)—ARS	530	1:2	3.5—7.5

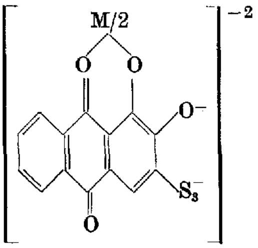
Table 14
Stability Constants of the ARS Chelates
pH 4.0; Temperature 25°

Chelate	log K	ΔG° K. Cals	Method
Gd (III)—ARS	8.6 ± 0.4	—11.9 ± 0.4	(a)
	8.6 ± 0.1	—11.9 ± 0.1	(b)
	8.7 ± 0.2	—12.0 ± 0.2	(c)
Tb (III)—ARS	9.1 ± 0.4	—12.6 ± 0.4	(a)
	9.0 ± 0.5	—12.4 ± 0.5	(b)
	9.2 ± 0.2	—12.7 ± 0.2	(c)
Yb (III —ARS	8.7 ± 0.5	—12.0 ± 0.5	(a)
	8.6 ± 0.2	—11.9 ± 0.2	(b)
	8.7 ± 0.2	—12.0 ± 0.2	(c)
Lu (III)—ARS	9.2 ± 0.4	—12.7 ± 0.4	(a)
	9.2 ± 0.5	—12.7 ± 0.5	(b)
	9.1 ± 0.2	—12.6 ± 0.2	(c)

Table 15
Analytical Applications of ARS Chelates
pH 4.0; Temperature 25°

Metal ion	Wavelength of study (mμ)	Range for adherence to BEER's law (p.p.m.)	Sensitivity (Sandell) γ/cm^2
Gd (III)	530	0.42—12.8	0.078
Tb (III)	503	0.42—12.9	0.070
Yb (III)	530	0.46—13.9	0.086
Lu (IIII)	530	0.46—14.0	0.086

The structure of the lanthanoid-ARS chelate is believed to be as follows:



The chelate is anionic as ascertained by the electrophoretic as well as by the ion exchange studies.

The present work has been able to throw light on the nature and characteristics of some coloured chelates of the lanthanoids and the chelate forming reactions described are being reported for the first time in this work. It has been observed that the order of the stability constants of the various lanthanoid chelates do not follow any particular sequence and hypothesis of their dependence on ionic charge and ionic radii is inadequate. It is, therefore, concluded that a large amount of data has to be accumulated in order to be able to generalize the magnitude of the stability constant values of the metal chelates of the lanthanoids.

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