

## A Spectrophotometric Study of the Chelates of Ammonium Aurintricarboxylate with Scandium, Yttrium, and Lanthanum\*

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The formation of a pink colour produced by the interaction of ammonium aurintricarboxylate (Aluminon) and scandium, yttrium, or lanthanum has been studied to determine the composition, stability and other characteristics of the chelates formed. The absorbance curves of the complexes show maxima at 535 m $\mu$  in all the chelates. The compositions of the chelates have been established by three different methods. The apparent stability constants of the chelates are estimated as  $10^{4.4}$ – $10^{4.9}$  for scandium,  $10^{4.4}$ – $10^{4.6}$  for yttrium, and  $10^{4.7}$ – $10^{4.9}$  for lanthanum at pH 5.5 and at 25°. The chelates are stable over a wide range of pH (i.e. 4.5 to 8.6). The maximum colour formation is attained at pH 5.5 when the mixtures contain greater than 4-fold excess of the reagent with respect to the metal solution and the colour intensity remains unaltered even after keeping the mixture for 12 hours at the room temperature. A tentative suggestion has been made for the position of the chelate ring in the chelates.

A comprehensive programme of work has been undertaken in these laboratories on the study of the chromogenic reactions of scandium, yttrium, lanthanum, and the lanthanoids and the reagents studied from this point of view include, Alizarin Red S<sup>1</sup>, Chrome Azurol S<sup>2</sup>, Thoron<sup>3</sup>, Chromotrope 2B<sup>4</sup>, 4,2-(pyridylazo) resorcinol<sup>5</sup>, Xylenol orange<sup>6</sup>, and 2-(*p*-sulphophenylazo)-1,8-dihydroxynaphthalene-3, 6-disulphonic acid (SPADNS)<sup>7</sup>.

Ammonium aurintricarboxylate (trivial name Aluminon, abbreviated as AAC) is well known as a chromogenic reagent for various inorganic cations<sup>8</sup>. This communication describes the studies on the composition, stability, and other properties of the chelate formed between Aluminon and scandium, yttrium, or lanthanum. The composition has been determined by various methods using absorbance measurements.

### EXPERIMENTAL

Absorbance and pH measurements were carried out as reported in earlier communications<sup>4</sup>.

Johnson Matthey samples of scandium chloride, yttrium chloride, and lanthanum chloride were dissolved in HCl (dil.) and the metal contents were estimated by the usual methods. An aqueous stock solution of AAC (B.D.H. indicator) was prepared.

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1. Munshi *et al.*, *Microchem. J.*, 1963, 7, 473.
2. Dey, *Microchim. Acta*, 1964, 414.
3. Sangal, *Chim. Anal.*, in press.
4. Sangal *et al.*, this *Journal*, 1963, 40, 275.
5. Munshi and Dey, *Anal. Chem.*, 1964, 36, 2003.
6. *Idem*, *Chemist Analyst*, 1964, 5, 105.
7. *Idem*, *Microchem. J.*, 1964, 8, 152.
8. Mukherji and Dey, *J. Colloid Sci.*, 1956, 13, 99.

All the experiments were performed in an air-conditioned room at  $25^{\circ} \pm 1^{\circ}$ . The total volumes of all the mixtures prepared for the measurements were kept 25 ml and the pHs were adjusted to 5.5 by addition of suitable amounts of HCl or NaOH. In the studies with lanthanum and yttrium, 5 ml of molar solution of mannitol was added to check precipitation of the complex.

#### DISCUSSION

*Behaviour of the Reagent as Colloidal Electrolyte.*—The reagent behaves as a colloidal electrolyte as reported earlier<sup>9</sup> and hence dilute solutions of AAC of the order of  $10^{-4}M$  and  $10^{-3}M$  were employed during these studies.

*Nature of the Complexes Formed.*—The method of Vosburgh and Cooper<sup>9</sup> was employed to determine the nature of the complexes formed in solution. Mixtures containing 0:1, 2:1, 1:1, 1:2, 1:3, and 1:4 ratios of metal to AAC were prepared, keeping the total volume at 25 ml in each case. Absorbance measurements were carried out between a range of 400  $\mu$  and 600  $\mu$ . The observations show that with all the metals only one complex is formed with AAC under the conditions of study, having  $\lambda_{max}$  at 535  $\mu$  in all the cases. The  $\lambda_{max}$  of the reagent at this pH is 515  $\mu$ .

*Effect of pH.*—Precipitation of the free acid (AAC) occurred at pH lower than 4. The maximum absorbance of a number of mixtures containing  $2.0 \times 10^{-4}M$  each of the reagent and the metals were noted at different pH values. Similar studies with yttrium and lanthanum were also performed. The results are recorded in Table I\*.

TABLE I

| Chelate. | pH range of stability. |
|----------|------------------------|
| Sr — AAC | 4.0 — 9.0              |
| Y — AAC  | 4.5 — 8.5              |
| La — AAC | 4.5 — 8.5              |

*Effect of Reagent Concentration.*—The absorbance values of mixtures of metal solutions ( $1.0 \times 10^{-4}M$ ) with varying ratios of AAC at pH 5.5 and at 533  $\mu$  showed that maximum colour formation was only attained when the mixtures contained greater than 4-fold excess of the reagent with respect to the metal solution.

*Stability of Colour at Room Temperature.*—Mixtures containing  $2.0 \times 10^{-4}M$  of metals and  $2.0 \times 10^{-4}M$  AAC at pH 5.5 retained the colour intensity even after 12 hours of standing at the room temperature.

*Composition of the Chelates.*—To estimate the empirical formula of the complex species formed under the present conditions the (i) method of continued variations, (ii) slope-ratio method, and (iii) mole-ratio method were employed\*\*.

For the first method, solutions of metal ion and AAC of the same concentration were mixed in varying proportions and the series of solutions thus prepared were adjusted to

9. *J. Amer. Chem. Soc.*, 1941, 63, 427; 1942, 64, 1630.

\* Fig. omitted.

\*\* For reference vide Dwivedi *et al.*, this issue p. 111.

pH 5.5 and absorbances were measured at 535 and 545 m $\mu$ . Fig. 1 ( $c$ =concentration of scandium,  $c'$ =concentration of AAC,  $p=c'/c$ ) represents a typical graph, showing the combining ratio of scandium to AAC as 1 : 1.

In the second method, two series of solutions were prepared: in the first series various amounts of metal ions (Sc, Y or La) were added to a large excess of AAC and in the second series, different quantities of AAC were added to a large excess of metal ions. The absorbances of the solutions were measured and plotted against the concentration of the variable component. The combining ratio of the complex is equal to the ratio of the slopes of the two straight lines, indicating the formation of 1 : 1 (Sc : AAC) species.

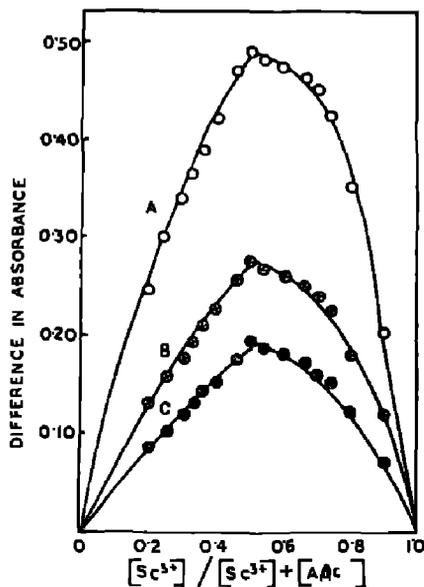


FIG. 1  
 $p=1.0$ .  $\lambda=535$  m $\mu$   
Conc. (a) in A—C are respectively 5.0, 2.5, and  $1.67 \times 10^{-4} M$ .

viz., (i) method of Dey and co-workers<sup>1011</sup>, (ii) mole-ratio method, and (iii) method of continued variations using nonequimolecular solutions. The results are shown in Table II. The free energy change of formation has also been calculated with the help of the expression:

$$\Delta G^{\circ} = -RT \ln K$$

the terms having their usual imports.

The composition of the chelates has also been confirmed by the mole-ratio method which suggests the formation of 1 : 1 (Sc : AAC) chelate in the solution.

Similarly the composition of the yttrium and lanthanum chelates with AAC was confirmed by all the aforementioned methods having 1 : 1 ratio (pH 5.5;  $\lambda=535$  m $\mu$ ).

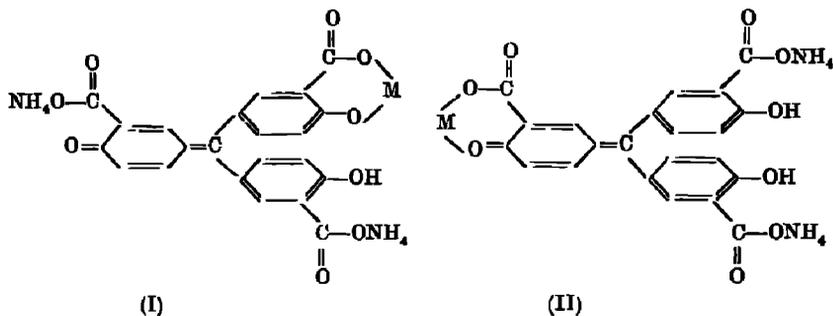
#### Evaluation of Stability Constants.—

The apparent stability constants of the chelates formed were calculated from the absorbance data by the three methods,

TABLE II

| Chelate. | Method. | log K.    | $\Delta G^{\circ}$ at 25° (kcal.). |
|----------|---------|-----------|------------------------------------|
| Sc — AAC | (i)     | 4.4 ± 0.2 | 6.0 ± 0.3                          |
|          | (ii)    | 4.9 ± 0.2 | 6.7 ± 0.3                          |
|          | (iii)   | 4.3 ± 0.1 | 5.9 ± 0.2                          |
| Y — AAC  | (i)     | 4.0 ± 0.2 | 5.3 ± 0.2                          |
|          | (ii)    | 4.6 ± 0.2 | 6.3 ± 0.2                          |
|          | (iii)   | 4.4 ± 0.1 | 6.0 ± 0.2                          |
| La — AAC | (i)     | 4.3 ± 0.1 | 5.9 ± 0.2                          |
|          | (ii)    | 4.5 ± 0.1 | 6.2 ± 0.2                          |
|          | (iii)   | 4.1 ± 0.1 | 5.6 ± 0.2                          |

*Suggestions on the Structure of the Chelate.*—Tentative suggestions have been made for the structure of the chelates with AAC. As it is evident from the structure of the reagent, co-ordination is possible in two ways; (i) either between the carboxylic oxygen and the adjacent phenolic oxygen or (ii) between the quinoid oxygen and the adjacent phenolic oxygen of the carboxylic group. The following would be the resulting structures.



If the co-ordination takes place according to (I), there would be an increase in the *pH* of the system, caused by dissociation of hydrogen as a result of chelation. On the other hand, if the chelation takes place as in (II), the *pH* of the mixture would remain unaltered.

It has been found that during chelation of Sc, Y, and La with AAC, an increase in acidity results in the system, indicating chelation as suggested by (I).

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10. Mukherji and Dey, *Anal. Chim. Acta*, 1956, 19, 324.

11. *Idem*, *J. Inorg. Nucl. Chem.*, 1958, 6, 314.