

918. Co-ordination Compounds between Ethylenediaminetetra-acetic Acid and Gallium, Indium, and Thallium.

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Co-ordination compounds of gallium, indium, trivalent thallium, and aluminium have been prepared crystalline, and their compositions determined. The solids contain one mol. of co-ordinated water. Potentiometric titration of their aqueous solutions with alkali hydroxide gives curves similar to that given by trivalent chromium or iron, showing that the co-ordinated water is capable of dissociating to a hydrogen ion and a hydroxy-complex anion. Under certain conditions, the co-ordinated water can be replaced by other donors including halogen or ammonia. Thus elements of Group IIIB form compounds with ethylenediaminetetra-acetic acid similar to those of aluminium, trivalent chromium, or ferric iron rather than to those of the rare-earth elements.

SCHWARZENBACH and BIEDERMANN¹ suggested, from results of potentiometric titration, that anionic complexes are formed between ethylenediamine-*NNN'*-tetra-acetic acid² (EDTA) and aluminium, chromium, and ferric iron in a 1 : 1 molar ratio and contain 1 mol. of co-ordinated water, which dissociates at pH 5—9 to give a hydrogen ion and a hydroxy-complex ion ($M^{III}Y \cdot OH$)²⁻ (Y = the EDTA radical, $C_{10}H_{12}O_8N_2^{4-}$). They further prepared a crystalline complex compound $HCrY \cdot H_2O$ which did not lose its water on prolonged heating at 110° *in vacuo*.

Tervalent cobalt forms a similar anionic complex;³ the co-ordinated water can be replaced by other donors, including halogens. The aquo-complex is, however, not stable enough to be obtained crystalline. Tervalent ions of the rare-earth elements, on the contrary, do not form such aquo-complex anions, although complex anions which contain other acid radicals are known.⁴

Little information was available concerning complex formation between EDTA and the trivalent metals of the gallium group. Flaschka and his co-worker⁵ used the EDTA complexes of indium and trivalent thallium in the analysis of both elements, tacitly assuming the formation of 1 : 1 compounds. Schwarzenbach, Gut, and Anderegg,⁶ in their extensive study on the stability constants of EDTA complexes with a variety of metal ions, gave the formation constants for the indium and the gallium complexes but did not state the composition of these complexes.

The present authors were of the opinion that the behaviour of trivalent ions of the gallium group towards EDTA could be compared with that of aluminium and of the rare-earth elements, since their ionic radii are between those of aluminium and the rare earths and their ionisation potentials are of comparable order. The complex compounds of gallium, indium, trivalent thallium, and aluminium with EDTA have therefore been prepared crystalline and their properties examined.

EXPERIMENTAL

Complex Compounds of Gallium.—Gallium nitrate, dissolved in water, was treated with an equivalent amount of disodium salt of EDTA and made strongly acidic with perchloric acid. *Monohydrogen aquoethylenediaminetetra-acetatogallium(III)* crystallised in a good yield on the addition of acetone (Found: Ga, 18.5; C, 31.8; total H, 4.0; loss at 110°, 0.2.

¹ Schwarzenbach and Biedermann, *Helv. Chim. Acta*, 1948, **31**, 459.

² Brintzinger and Hesse, *Z. anorg. Chem.*, 1942, **249**, 113; Brintzinger, Thiele, and Miller, *ibid.*, 1943, **251**, 285.

³ Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.

⁴ Marsh, *J.*, 1950, 1819; Vickery, *J.*, 1951, 1817.

⁵ Flaschka, *Mikrochem. Mikročim. Acta*, 1952, **40**, 42; Flaschka and Amin, *Z. analyt. Chem.*, 1953, **140**, 6.

⁶ Schwarzenbach, Gut, and Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937; Schwarzenbach and Freitag, *ibid.*, 1951, **34**, 1503.

HGaC₁₀H₁₄O₉N₂ requires Ga, 18.5; C, 31.9; H, 4.0; H₂O, 0%). The aqueous solution of this compound was neutralised with sodium or potassium hydroxide, kept in a vacuum-desiccator until small crystals were formed on the surface, then treated with acetone to precipitate the tetrahydrated *sodium* or dihydrated *potassium aquoethylenediaminetetra-acetato*gallium as prisms (Found: Ga, 15.1; Na, 5.0; C, 26.6; total H, 4.7; loss at 110°, 15.7. NaGaC₁₀H₁₄O₉N₂·4H₂O requires Ga, 14.8; Na, 4.9; C, 25.5; H, 4.6; 4H₂O, 15.3%. Found: Ga, 15.6; K, 9.0; C, 27.9; total H, 3.8; loss at 110°, 8.2. KGaC₁₀H₁₄O₉N₂·2H₂O requires Ga, 15.5; K, 8.7; C, 26.6; H, 4.0; 2H₂O, 8.0%). The water of crystallisation of both alkali salts was lost at 110°, but the co-ordinated water not until 250° where the decomposition of the organic component began.

Complex Compounds of Indium.—Freshly precipitated indium hydroxide, free from electrolytes, was boiled with an equivalent amount of EDTA until an almost clear solution was obtained. The mixture was filtered, made acid with perchloric acid, and treated with acetone. Colourless *monohydrogen aquoethylenediaminetetra-acetato*indium(III) was precipitated; it was washed with acetone and dried between filter paper (Found: In, 27.1; C, 29.1; total H, 4.0; loss at 200°, 4.9. HInC₁₀H₁₄O₉N₄ requires In, 27.3; C, 28.5; H, 3.6; H₂O, 4.3%). When equivalent amounts of indium hydroxide, EDTA, and alkali hydroxide were boiled, reaction was faster. Filtration, evaporation, and treatment with acetone gave the dihydrated *sodium* or monohydrated *potassium aquoethylenediaminetetra-acetato*indium (Found: In, 24.2; Na, 4.9; C, 25.1; total H, 3.8; loss at 110°, 7.5; further loss at 200°, 3.8. NaInC₁₀H₁₄O₉N₄·2H₂O requires In, 23.9; Na, 5.0; C, 25.0; H, 3.8; 2H₂O, 7.5; H₂O, 3.8%. Found: In, 24.2; K, 7.75; C, 24.9; total H, 3.7; loss at 200°, 7.75. KInC₁₀H₁₄O₉N₄·H₂O requires In, 24.0; K, 8.2; C, 25.1; H, 3.35; H₂O + H₂O, 7.55%). The *ammonium salt monohydrate* is obtained when the monohydrogen complex is treated successively with aqueous ammonia (1 equiv.) and acetone (an excess of ammonia should be avoided; otherwise the salt would be contaminated by the ammine complex) (Found: In, 25.4; NH₃, 3.2; loss at 110°, 0.15; further loss at 200°, 8.3. NH₄InC₁₀H₁₄O₉N₂·H₂O requires In, 25.1; NH₃, 3.7; H₂O + H₂O, 7.9%). The *caesium salt trihydrate* is similarly obtained (Found: In, 18.8; Cs, 20.2; C, 19.8; total H, 3.7; loss at 110°, 11.8. CsInC₁₀H₁₄O₉N₂·3H₂O requires In, 18.2; Cs, 21.9; C, 19.8; H, 3.3; H₂O + 3H₂O, 12.0%).

When the sodium salt of the aquo-complex was dissolved in a warm solution of sodium bromide (45%) and set aside for a few days, prisms of *disodium bromoethylenediaminetetra-acetato*indium(III) *tetrahydrate* were precipitated. They were washed with water-acetone saturated with sodium bromide and then with acetone (Found: In, 19.2; Na, 7.9; Br, 13.1; loss at 110°, 13.1. Na₂InC₁₀H₁₃O₈N₂Br·4H₂O requires In, 19.1; Na, 7.65; Br, 13.3; 4H₂O, 12.0%). *Diammonium chloroethylenediaminetetra-acetato*indium(III) *dihydrate* was obtained in cubes by boiling equivalent amounts of indium hydroxide and EDTA in a concentrated solution of ammonium chloride, made basic with ammonia [Found: In, 22.8; NH₃, 6.7; Cl, 6.5; loss at 110°, 7.1. (NH₄)₂InC₁₀H₁₂O₈N₂Cl₂·2H₂O requires In, 22.5; NH₃, 6.95; Cl, 6.7; 2H₂O, 7.1%]. Plates of *ammonium amminoethylenediaminetetra-acetato*indium(III) *monohydrate* were precipitated on treatment of a solution of the ammonium salt of the aquo-complex in aqueous ammonia with acetone [Found: In, 25.2; loss at 105°, 4.3; NH₃, 7.5. NH₄InC₁₀H₁₂O₈N₂·NH₃·H₂O requires In, 25.2; NH₃, 7.5; H₂O, 3.95%]. All of these halogeno- and ammino-complexes are soluble in water and rapidly hydrolysed to the aquo-complex anion (InY·H₂O)⁻ and bromide, chloride, or ammonium ions. The water of crystallisation of these compounds is removed at 110°.

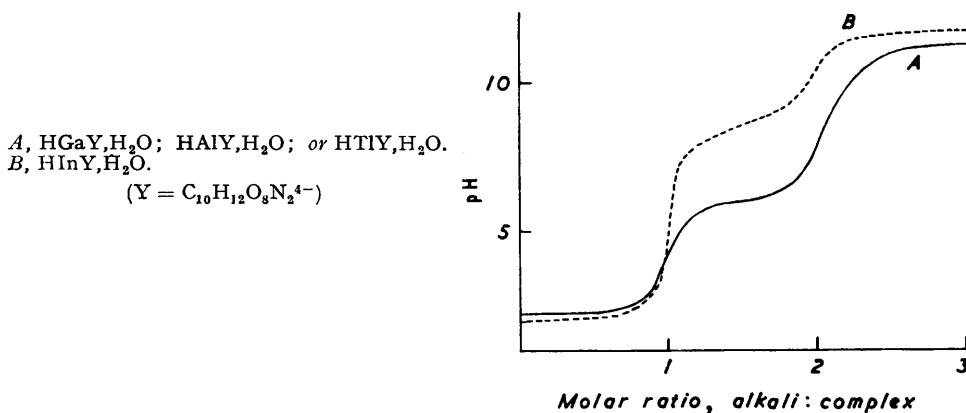
Complex Compound of Tervalent Thallium.—Metallic thallium was dissolved in concentrated nitric acid and oxidised with chlorine. The product was treated with aqueous ammonia, yielding a dark brown precipitate of the hydroxide, which was dissolved in nitric acid. Aqueous solution of the equivalent amount of disodium salt of EDTA was gradually added with stirring. Colourless *monohydrogen aquoethylenediaminetetra-acetato*thallium(III) was precipitated on the addition of acetone (Found: Tl, 39.6; C, 24.3; H, 3.3. HTlC₁₀H₁₄O₉N₂ requires Tl, 40.0; C, 23.5; H, 3.0%). This began to char at about 95° and gradually lost weight until complete decomposition of the organic residue occurred.

Complex Compounds of Aluminium.—Freshly precipitated aluminium hydroxide was boiled with an equivalent amount of EDTA until a clear solution was obtained, which was filtered, evaporated, and treated with ethanol to precipitate prisms of *monohydrogen aquoethylenediaminetetra-acetato*aluminium(III) (Found: Al, 8.2; C, 36.6; H, 5.1. HAIC₁₀H₁₄O₉N₂ requires Al, 8.1; C, 36.0; H, 4.5%). An aqueous solution of this compound was exactly neutralised, kept in a vacuum-desiccator until crystals were formed, and treated with acetone

to precipitate prisms of *sodium aquoethylenediaminetetra-acetatoaluminium(III) tetrahydrate* or the *potassium salt dihydrate* (Found: Al, 6.40; Na, 5.9; C, 29.7; total H, 5.1; loss at 110°, 16.5. $\text{NaAlC}_{10}\text{H}_{14}\text{O}_9\text{N}_2 \cdot 4\text{H}_2\text{O}$ requires Al, 6.3; Na, 5.4; C, 28.1; H, 5.2; $4\text{H}_2\text{O}$, 16.8%. Found: Al, 6.8; K, 8.5; C, 31.7; total H, 4.3; loss at 110°, 9.0. $\text{KAlC}_{10}\text{H}_{14}\text{O}_9\text{N}_2 \cdot 2\text{H}_2\text{O}$ requires Al, 6.6; K, 9.6; C, 29.4; H, 4.4; $2\text{H}_2\text{O}$, 8.8%). Satisfactory values for carbon were obtained with the anhydrous *aquo-salts* (Found: C, 34.1. $\text{NaAlC}_{10}\text{H}_{14}\text{O}_9\text{N}_2$ requires C, 33.7%. Found: C, 32.5. $\text{KAlC}_{10}\text{H}_{14}\text{O}_9\text{N}_2$ requires C, 32.3%).

The monohydrogen complexes of these metals are sparingly soluble in water whilst the salts are very soluble but not hygroscopic. None of them is soluble in organic solvents, including those having higher dielectric constants. Aqueous solutions of anionic complexes of gallium, indium, and aluminium fail to show ordinary reactions of the metal ions. On the addition of a concentrated solution of alkali hydroxide, however, the indium complex gives a colourless precipitate of the hydroxide. An aqueous solution of the thallic complex appears to be less stable towards reagents. On the addition of alkali hydroxide the brown hydroxide is precipitated. It oxidises potassium iodide to iodine equivalent in amount to the thallium. No significant reduction is observed, however, on the treatment with sulphur dioxide.

Potentiometric Titration.—Potentiometric titration curves of the aqueous solution of the monohydrogen complexes of gallium, indium, thallium, and aluminium with alkali hydroxide, followed by the use of a glass electrode, are shown in the Figure. Similar curves were obtained



at a constant ionic strength in 0.1M-potassium nitrate. The curves for the alkali salts are respectively identical with the second half of those in the Figure, regardless of the cationic component of the complex salts. The solution of sodium bromo-EDTA-indium(III) gives a curve identical with that of the aquo-complex, whilst curves of ammonium salts of aquo-, chloro- and amino-EDTA complexes are less distinctive.

Absorption Spectra.—Aqueous solution of the complexes of gallium, indium, and aluminium are non-absorbing in the range 950—220 $\text{m}\mu$ (absorption of EDTA itself starts at 220 $\text{m}\mu$); the absorption of the thallic complex remarkably increases below 320 $\text{m}\mu$. Generally it is believed that the greater the stability of a chelate compound, the shorter the wavelength at which the characteristic absorption cuts off.

Analysis.—For analysis of metallic components of the complex compounds, the sample was decomposed with sulphuric and nitric acid. The hydroxides of gallium, indium, and aluminium were precipitated from acid solution with aqueous ammonia and ignited to oxides. Tervalent thallium was reduced to the univalent state with sulphur dioxide and precipitated with chromate ions in ammoniacal solution. Alkalis were determined in the filtrate from the hydroxides by the usual method. Bromide and chloride were precipitated with a known amount of silver nitrate; the excess of the latter was back-titrated with potassium thiocyanate (iron alum as indicator). Ammonia was determined by the Kjeldahl method. Since the halogeno-complex anions are very rapidly hydrolysed in an aqueous solution, no special procedure was required for the displacement of halogens. The analyses of carbon and hydrogen were carried out mainly by Mr. A. V. Winter, whom the authors thank. They thank also Dr. Judith Grenville-Wells for her help in crystallographic measurement.

DISCUSSION

From the titration curve it is seen that the anionic complexes of EDTA with gallium, indium, and thallium in aqueous solution contain one mol. of co-ordinated water, which as with chromium, ferric iron, and aluminium, dissociates to give a hydrogen ion. The fact that one mol. of water is removed with difficulty from the crystals of the complexes supports the view that it is held in the ligand also in the solid state. It was thus concluded that the co-ordination compounds of the gallium group of elements with EDTA are similar to those of aluminium (and of ferric iron and chromium) rather than to those of the rare-earth elements.

Since the formation of the complexes is extensive enough,⁶ apparent values of dissociation constants for protons calculated as shown below could provide an approximation to

Comparison of EDTA complexes of the Group IIIB elements.

	Al	Ga	In	Tl
r (Å) ^a	0.57	0.62	0.92	1.05
K ^b	1.3×10^{16}	1.8×10^{20}	8.9×10^{24}	—
K_1 ^c	0.10×10^{-2}	3.9×10^{-2}	$>1 \times 10^{-1}$	0.20×10^{-2}
K_2 ^d	0.69×10^{-6}	1.2×10^{-6}	1.6×10^{-9}	0.32×10^{-6}

^a Ionic radius (from Pauling's table). ^b Formation constants of the complex anion (measured by Schwarzenbach ⁶). ^c Apparent dissociation constants of proton from the monohydrogen complex at 15°: $[H^-][MY \cdot OH_2^-]/[HMY \cdot OH_2]$. ^d Apparent dissociation constants of proton from the co-ordinated water at 15°: $[H^-][MY \cdot OH_2^-]/[MY \cdot OH_2^-]$.

the affinity between the proton and the anionic complex. K_1 and K_2 were calculated from the data of potentiometric titration on the assumption that only a negligible amount of hydrogen ion is provided by the dissociation of free EDTA.

It appears as if K_1 , which can be a criterion of the affinity between proton and the co-ordinated EDTA radical, increases with increase in the formation constant of the anionic complex as given by Schwarzenbach and his co-workers. The K value for thallic complex has not been measured as yet; it can be predicted, however, that it would be significantly smaller than that for indium. Such a decrease in stability is also observed in the series magnesium, zinc, cadmium, and mercury. The ease with which the thallic complex is reduced to the thallic state and decomposed by heat supports this view, too. This could be correlated with the value of ionisation potential; the latter decreases with increasing ionic radius in a sub-group of the Periodic Table, but mercury and thallium have greater values than those of cadmium and indium, respectively.

The K_2 values appear to decrease with increase in the ionic radius. The smaller the ionic radius, the stronger the interaction between the metal ion and the co-ordinated water. The electron cloud of the oxygen atom might be so attracted by the metal ion that the electrolytic dissociation of proton is promoted to give a greater K_2 value. This also accounts for the loose combination of water in the indium complex. The heaviest member of the sub-group again shows an irregular behaviour.

The fact that the monohydrogen complexes of gallium and aluminium and their sodium and potassium salts have respectively the same numbers of water molecules of crystallisation suggests that they may form isomorphous crystals. A comparison by the Debye-Scherrer method disclosed that they formed very similar crystals although it was not certain that they were isomorphous.

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