Bull. Chem. Soc. Jpn., 57, 3426—3429 (1984) [Vol. 57, No. 12

Stability Constants of Scandium Complexes. II. Dicarboxylate Complexes Species

Hisako Itoh, Yukihiro Ikegami, and Yasuo Suzuki*

Department of Industrial Chemistry, Faculty of Engineering, Meiji University, Higashi-mita, Tama-ku, Kawasaki 214

(Received April 14, 1984)

The stability constants of scandium complexes with malonate, maleate, itaconate, glutarate, adipate, and succinate ligands were determined titrimetrically at 25.0 °C and at an ionic strength of 0.1. The chelate effect was negligible for the stability of the scandium complexes with the dicarboxylate ligands studied in contrast with the lanthanoid complexes. The complex formation of scandium might be explained by an electrostatic ionic bond similar to ones exhibited in the lighter rare-earth complexes, due to linear relationships between the stability constants and the ionic potential Z^2/r.

Scandium has been known for almost one hundred years, although its chemistry, particularly its coordination chemistry, has been little studied. In 1970, a review[1)] was given on its coordination chemistry. The lack of attention has probably been due to the difficulty, until recently, of obtaining a pure source, though the metal and the oxide are now commercially available in high purity.

In our previous paper,[2)] stability constants of scandium complexes with some monobasic acids were reported and compared with those of the lanthanoid complexes. The constants of the scandium complexes were appreciably greater than those of the corresponding lanthanoid complexes, as expected from the smaller ionic radius. The scandium complexes were thought to be similar to the lighter rare-earth complexes with regard to coordinating characteristics and to the degree of cationic hydration. In this study, the stability constants of scandium complexes with some dicarboxylic acids were determined titrimetrically and compared with those of the lanthanoid complexes.

Experimental

Reagents and Apparatus. A scandium nitrate solution was prepared as described previously.[2)] Stock solutions of dicarboxylic acids were prepared using analytical reagents and were standardized by potentiometric titration with a standard solution of sodium hydroxide. The pH-measuring system consisted of an Orion model 701A digital pH/mV meter, an Orion 91-01 glass electrode and a Beckman 39400 reference electrode. The instrument is capable of measuring the pH of a solution with an accuracy of 0.001 unit.

Procedure and Calculations. To determine the stability constants, solutions containing a ligand acid, scandium nitrate and potassium nitrate were titrated with standard sodium hydroxide. The solutions were stirred continuously and the temperature was maintained at 25.0°C during the titrations. Sufficient time was allowed between successive additions of the base in order to obtain constant pH readings. The titrations were continued until precipitation occurred. The constants were calculated by the Bjerrum method.[3)] The values of $\bar{n}$ and [A] calculated by the following equations were taken at or near $\bar{n}$=0.5 and 1.5,

$$[\mathrm{A}] = \frac{(2-a)A_\mathrm{t}-[\mathrm{H}]+[\mathrm{OH}]}{2[\mathrm{H}]^2/K_{\mathrm{a}1}K_{\mathrm{a}2}+[\mathrm{H}]/K_{\mathrm{a}2}}$$

$$\bar{n} = \frac{A_\mathrm{t}-([\mathrm{H}]^2/K_{\mathrm{a}1}K_{\mathrm{a}2}+[\mathrm{H}]/K_{\mathrm{a}2}+1)[\mathrm{A}]}{M_\mathrm{t}},$$

where [A] is the concentration of free ligand acid, $\bar{n}$ is the ligand number, A_t and M_t are the total concentration of the ligand acid and scandium metal, respectively, $K_{\mathrm{a}1}$ and $K_{\mathrm{a}2}$ are the first and second dissociation constants of the acid, respectively, and a is the mole number of the sodium hydroxide added to one mole of the ligand acid. The acid-dissociation constants were determined in a similar way to the stability constants, as described above.

Results and Discussion

Depending on the basicity and the content of hydroxyl and iminodicarboxyl groups, organic ligands exhibit different stabilities and different numbers of binding sites. When only carboxyl and hydroxyl groups are present, the ligands are usually bidentate, tridentate and, in some cases, monodentate. Monobasic acids, including those containing hydroxyl groups, form complexes of the type ScL^{2+}, dibasic acids form ScL'^{+}, while the formation of the acid ion ScHL''^{+} is characteristic of tribasic acids.

The acid-dissociation constants obtained are listed in Table 1. The experimental data for the titrations of the stability constants are shown as plots of $\bar{n}$ *vs.* log[A]

Table 1. Dissociation constants of dicarboxylic acids

Acid	$\mathrm{p}K_{\mathrm{a}1}$	$\mathrm{p}K_{\mathrm{a}2}$
Malonic acid	2.69	5.48
Maleic scid	1.84	5.83
Itaconic acid	3.68	5.23
Glutaric acid	4.19	5.09
Adipic acid	4.29	5.09
Succinic acid	4.00	5.29

Table 2. Stability constants of scandium complexes

Acid	log K_1		log K_2	
	This work	Previous work	This work	Previous work
Malonic acid	6.78	5.87[4)]	5.12	4.25[4)]
Maleic acid	5.98	5.34[5)]	4.27	
Itaconic acid	4.77		4.00	
Glutaric acid	5.21	4.82[6)]	3.70	
Adipic acid	5.25		3.50	
Succinic acid	5.55		3.88	

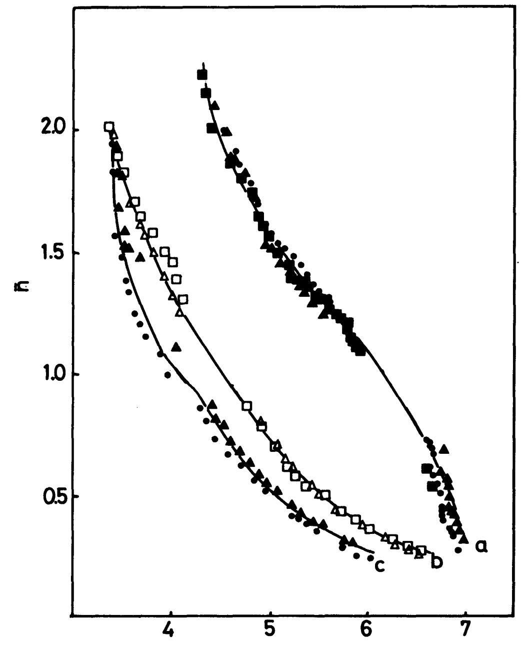

Fig. 1. Formation curves of scandium complexes. I. a: Malonate, b: Succinate, c: Glutarate.

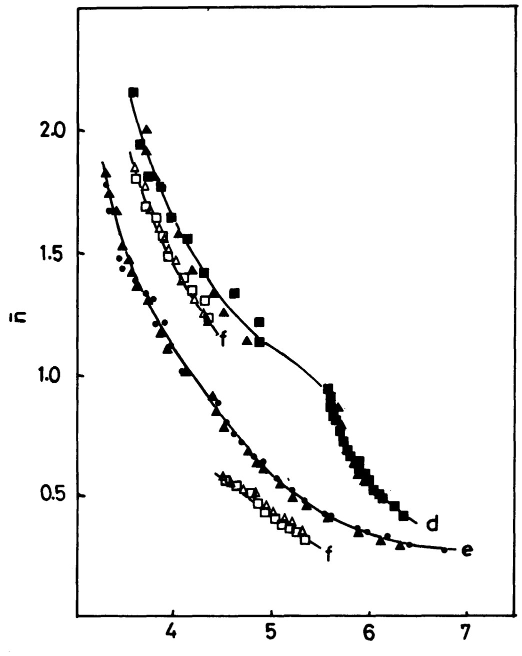

Fig. 2. Formation curves of scandium complexes. II. d: Maleate, e: Adipate, f: Itaconate.

in Figs. 1 and 2. In the [A]-region investigated, the first and second complexes were formed and no evidence for the formation of higher complexes was found. Acid complexes were formed for the itaconato complexes, as can be seen from the formation curves and from the stability constants[4] of the lanthanoid-itaconato complexes.

The stability constants obtained are listed in Table 2, together with previously reported values.[5–7] The values of log K_1 for scandium complexes of some mono- and dicarboxylate ligands are plotted as a function of pK_{a1} for the monocarboxylates and pK_{a2} for the dicarboxylates in Fig. 3. The plots of mono- and dicarboxylate ligands are located on the same straight line, indicating that the chelate effect would be negligible for the scandium complexes and that the hydroxyl groups play an important role in the formation of scandium complexes. The difference of log K_1 of two lines is approximately 3.5, corresponding to a hydrogen-bond energy of about 21 kJ mol^{-1}. The greater stability of ligands containing OH groups compared with those without OH groups would contribute to the intermolecular hydrogen bond between the OH groups and the carboxylate oxygen of the former ligands.

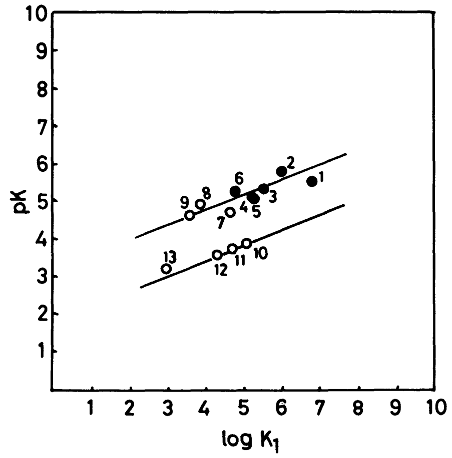

Fig. 3. Relation between the values of log K_1 and the pK_1 (of the monobasic ligands) or pK_2 (of the dibasic ligands).
1: Malonate, 2: Maleate, 3: Succinate, 4: Glutarate, 5: Adipate, 6: Itaconate, 7: Isobutyrate, 8: Propionate, 9: Acetate, 10: α-Hydoxyisobutyrate, 11: Glycolate, 12: D-Gluconate, 13: Mandelate.

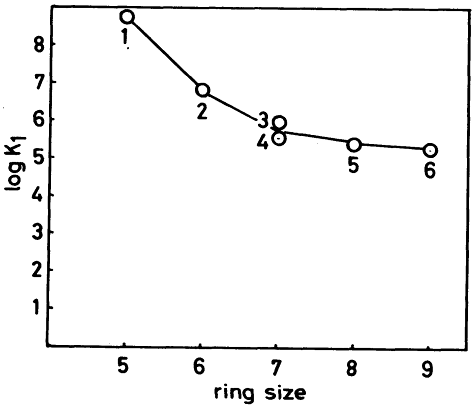

Fig. 4. Relation between stability constants and ring size.
1: Oxalate, 2: Malonate, 3: Maleate, 4: Succinate, 5: Glutarate, 6: Adipate.

The relationship between the stability constants and ring size is shown in Fig. 4. The stability constant of an oxalato complex (having a five-membered ring)

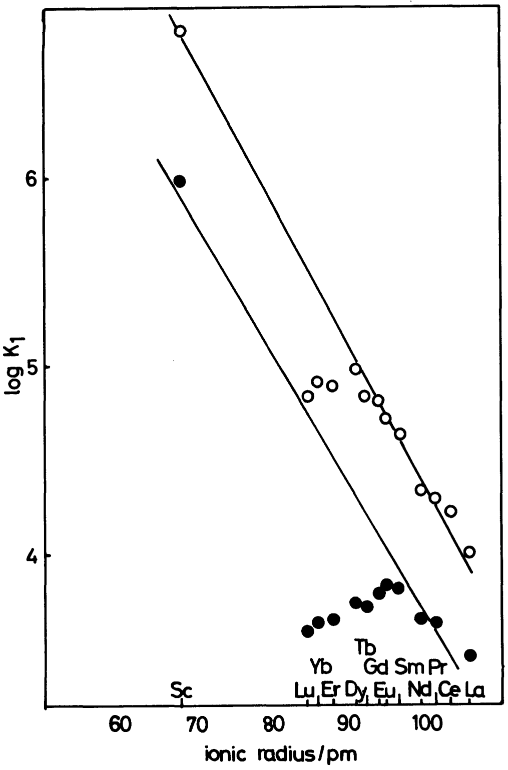

Fig. 5. Relation between stability constants and ionic radius.
○: Malonate, ●: Maleate.

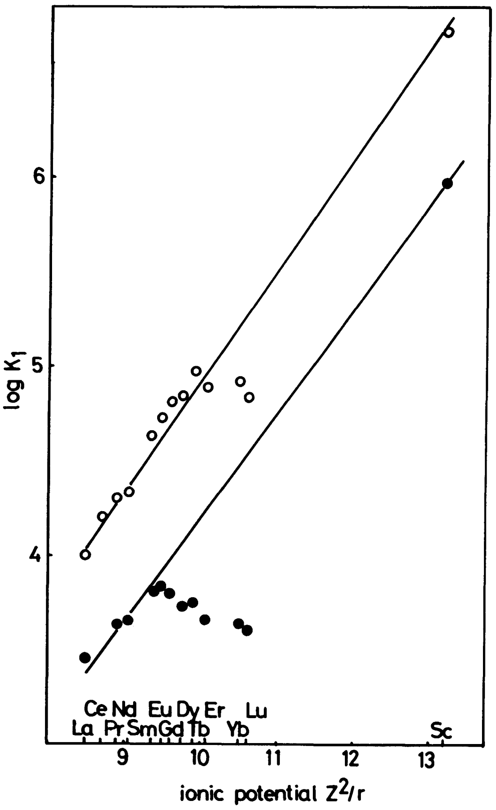

Fig. 6. Relation between stability constants and ionic potential (Z^2/r).
○: Malonate, ●: Maleate.

gives the greatest values (decreasing with increasing ring size). The greater stability of the malonato complex compared to the maleato, glutarato and adipato complexes indicates that the malonato complex forms six-membered rings while the maleato, glutarato, and adipato complexes have seven-, eight-, and nine-membered rings, respectively.

The relation between the stability constant (log K_1) of the scandium and lanthanoid complexes and the ionic radius are shown in Fig. 5. As well as the monobasic acids described before,[2] the stability constants of the scandium complexes with malonic and maleic acids are on the extrapolated lines of the lighter rare-earth complexes rather than those of the heavier rare earths. In the case of the itaconato, glutarato, adipato and succinato complexes, such relationships were not obtained due to a lack of the values for the corresponding lanthanoid complexes.

When a bond between metal and a ligand is purely ionic, the bond strength increases linearly with increasing ionic potential Z^2/r (Z: ionic charge, r: ionic radius), according to Born's equation. The relationships between the stability constants of the rare-earth complexes and the ionic potential are shown in Fig. 6. The linearity was obtained for the scandium and lighter rare-earth complexes, but not for the heavier rare-earth complexes.

Since there is a regular decrease in the crystal radii of rare-earth metal ions, simple electrostatic theory predicts a direct relationship betweeen the atomic number of the rare-earth ion and the stability constants. In nearly all complexes which have been studied, this relationship was precisely found for the values of log K_1 for complexes of the lighter rare earths. This simple relationship was, however, not generally found when the heavier rare-earth ions were considered. The trends in the stability constants for the heavier rare-earth elements can be divided qualitatively into three types. The first group contains those ligands for which there is a regular increase in the values of the stability constants. This does not imply that these ligands follow the simple electrostatic model, since the slope of a plot of log K_1 *vs.* r is usually not the same as for the lighter rare earths. Ligands for which this trend is observed are glycolic, α-hydroxyisobutyric, and mandelic acids. The only obvious similarity among these ligands is that each has at least one OH group. The ligands in the second classification form complexes for which the stability constants of the heavier rare earths have nearly the same values from gadolinium to lutetium. These ligands are acetic, propionic and isobutyric acids. The third group contains dicarboxyllic acids, such as malonic and maleic acids. The stability-constant values for the complexes of these ligands increase with the first elements beyond gadolinium and then show a slight decrease to lutetium. The position of scandium with respect to the relationship between the stability constant and ionic radius is of interest.

The studies with lanthanoid perchlorates and oxygen donor ligands have shown that the coordination number varies with ionic size (values from six to twelve being reported).[8–14] In view of the smaller size of the scandium ion compared with any of the trivalent lanthanoid ions, scandium exhibits a maximum coordination number of six on the low end of the range observed for the heavier rare earths.

The complex formation of scandium with any of the three types of ligands might be explained by an electrostatic ionic bond similar to ones exhibited in the lighter rare-earth complexes, although the coordination number of scandium differs from the lighter rare earths. Other factors besides the purely electrostatic bond might be incorporated in the complex formation of the heavier rare earths.

References

1) G. A. Melson and R. W. Stotz, *Coord. Chem. Rev.*, **7**, 133 (1971).

2) H. Itoh, N. Itoh, and Y. Suzuki, *Bull. Chem. Soc. Jpn.*, **57**, 716 (1984).

3) J. Bejerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen (1957).

4) H. Schurmans, H. Thun, F. Verbeek, and W. Vanderleen, *J. Elelctroanal. Chem.*, **38**, 209 (1972).

5) I. Grenthe, G. Gordhammar, and E. Rundcrantz, *Acta Chem. Scand.*, **23**, 93 (1969).

6) I. M. Korenman and N. V. Zaglyadimova, *Zhur. Neorg. Khim.*, **18**, 2774 (1973).

7) E. I. Chubakova and N. A. Skorik, *Russ. J. Inorg. Chem.*, **18**, 1446 (1973).

8) V. N. Krishnamurthy and S. Sonndararajan, *J. Inorg. Nucl. Chem.*, **29**, 517 (1967).

9) F. N. Krishnamurthy and S. Sonndararajan, *Can. J. Chem.*, **45**, 189 (1967).

10) F. Kutek, *Collect. Czech. Chem. Commun.*, **33**, 1341 (1968).

11) J. O. Edwards, R. J. Goetsch, and J. A. Stritar, *Inorg. Chim. Acta*, **1**, 360 (1967).

12) T. Moeller and G. Vincentini, *J. Inorg. Nucl. Chem.*, **27**, 1477 (1965).

13) D. M. Mehs and S. K. Madan, *J. Inorg. Nucl. Chem.*, **30**, 3017 (1968).

14) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B.*, **25**, 925 (1969).