Thermodynamic Properties of Rare Earth Complexes

VII. Free Energy, Enthalpy, and Entropy Changes for the Formation of Scandium(III) Diglycolate, Dipicolinate, and Malonate Complexes at 25.00°C

INGMAR GRENTHE and EVA HANSSON

Division of Physical Chemistry, Chemical Center, University of Lund, Box 740, S-220 07 Lund 7, Sweden

The changes in free energy, enthalpy, and entropy for the formation of scandium(III) malonate, diglycolate, and dipicolinate complexes have been determined. All data refer to a temperature of 25.00°C and a sodium perchlorate medium of the total sodium ion concentration 1.00 M for the malonate and diglycolate systems and 0.50 M for the dipicolinate systems. The changes in free energy were computed from stability constants determined by standard potentiometric methods. The first stability constant in the diglycolate and dipicolinate systems was determined by a calorimetric competition method. The enthalpy changes were obtained by a direct calorimetric determination of heats of complex formation. The entropy changes were calculated by using the relationship

$$\Delta G_j^\circ = \Delta H_j^\circ - T\Delta S_j^\circ$$

The data obtained are compared with corresponding data for the lanthanum series.

The changes in free energy, enthalpy, and entropy for the formation of various rare-earth carboxylate complexes have been reported in a number of communications from this laboratory.[1-6] The variations of these thermodynamic quantities within the lanthanoids have been described as a result of the decreasing ionic radius of the central ion and the geometrical requirements of the ligand. In this investigation we have studied the complex formation between scandium(III) and the tridentate ligands diglycolate and dipicolinate and the bidentate ligand malonate.

Scandium(III) has a similar outer electron shell configuration as the tervalent lanthanoids but a considerably smaller ionic radius ($r_{Sc(III)} = 0.73$ Å).[7] A study of the changes in free energy, enthalpy, and entropy for various scandium(III) complex formation reactions gives more information about the influence of the radius of the central ion upon the complex formation.

A suitable method for determining the stability constants is one of the potentiometric standard methods for the determination of the concentration of free ligand by using protons or metal ions as competitors for the ligand. Protons were used as competitors in the diglycolate and malonate measurements and copper(II) ions in the dipicolinate measurements. The scandium diglycolate and dipicolinate complexes could be expected to be so strong relative to the corresponding proton and copper systems that the determination of the first stability constant would be difficult or even impossible. These constants were instead determined by a calorimetric competition method.

The various heats of formation were determined by using the calorimetric titration procedure described by Gerding *et al.*[8] All solutions contained free perchloric acid in amounts sufficient to suppress the hydrolysis of the central ion. This means that proton-ligand complexes are formed simultaneously with the scandium complexes during the calorimetric titrations with diglycolate and malonate. Thus the composition of the solution at the various stages of the titrations had to be determined from [H]-measurements and the heats measured were then corrected for the heats arising from the formation or disruption of the proton complexes. For the dipicolinate complexes the bonding is expected to be so strong that protons can not compete for the ligand when $\bar{n} < 2$.

All measurements were performed using a constant sodium ion concentration. In the diglycolate and malonate solutions this concentration was equal to 1.00 M and in the dipicolinate solutions equal to 0.50 M. Both the potentiometric and the calorimetric titrations were made at 25.00°C.

NOTATION AND GENERAL EQUATIONS

The notation and general calculation procedure is the same as described before.[1-3]

The following equations are valid when only mononuclear and nonacid complexes of the type MA_j are formed

$$X([A]) = \sum_{j=0}^{N} \beta_j [A]^j \tag{1}$$

$$\ln X([A]_j) = \int_0^{[A]_j} \frac{\bar{n}}{[A]} \, d[A] \tag{2}$$

$$\ln \frac{[A]_0}{[A]} = \int_{X_j}^{X_0} \frac{1}{\bar{n}} \, d\ln X \tag{3}$$

$$\Delta h_v = \sum_{j=1}^{N} \sum_{k=1}^{j} \alpha_j \Delta H_k^\circ \tag{4}$$

$$\gamma_1 = \frac{\Delta h_v X([A])}{[A]} \tag{5}$$

$$\gamma_n = \frac{\gamma_{n-1} - (\gamma_{n-1})_{[A]=0}}{[A]} = \sum_{j=1}^{N} \sum_{k=1}^{j} \beta_j [A]^{j-n} \Delta H_k^\circ \qquad (6)$$

In the above formulae $\bar{n}$, [A], and β_j are replaced by $\bar{n}_H$, [H], and δ_j, respectively, in dealing with the proton complexes.

EXPERIMENTAL

Chemicals used. Scandium perchlorate was prepared by dissolving the oxide (Johnson, Matthey & Co., 99.99 %) in warm perchloric acid. A 0.2 M stock solution was prepared and analysed for scandium by titration with EDTA.[9] The hydrogen ion concentration of the solution was determined potentiometrically and was made about 0.05 M to avoid hydrolysis.[10]
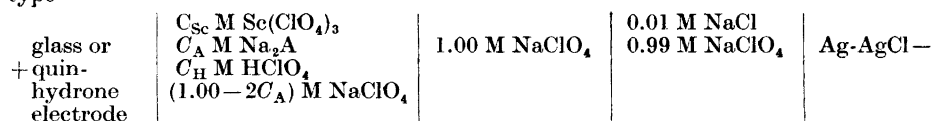
A stock solution of copper perchlorate was prepared according to Fronæus[11] and was analysed by titration with EDTA using murexide as indicator.

Sodium perchlorate was prepared from perchloric acid (Baker's analysed) and sodium carbonate (Merck *p.a.*).

The dicarboxylic acids were purified by recrystallization: dipicolinic acid (Fluka, purum) from water, diglycolic acid (Fluka, puriss) from ethyl acetate, and malonic acid (Fisher Sci. Co., *p.a.*) from diethyl ether. The equivalent weights were determined by alkalimetric titration and were all found to agree with the theoretical values within 0.2 %. Stock solutions of the disodium salts were prepared by neutralization of the acids with sodium hydroxide. The various buffers were then obtained by mixing appropriate amounts of these stock solutions with perchloric acid.

A 2 % liquid copper amalgam was prepared by electrolysis of an acid copper sulphate solution using mercury (Merck *p.a.*) as cathode. The Ag−AgCl electrodes were prepared according to Brown.[12]
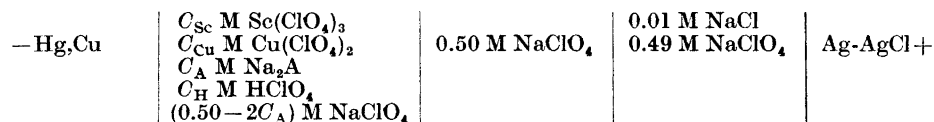
Potentiometric determination of stability constants. The stability constants δ_j of the proton ligand complexes and the stability constants for the scandium malonate and diglycolate complexes were determined by measuring the emf of galvanic cells of the type

glass or + quin- hydrone electrode	C_{Sc} M Sc(ClO$_4$)$_3$ C_A M Na$_2$A C_H M HClO$_4$ (1.00 − 2C_A) M NaClO$_4$	1.00 M NaClO$_4$	0.01 M NaCl 0.99 M NaClO$_4$	Ag-AgCl−

The solution in the left half cell was prepared by adding small amounts of a solution T from a burette to a known volume of a solution S. These solutions had the following compositions: S: C_{Sc} M Sc(ClO$_4$)$_3$, $C_{H(S)}$ M HClO$_4$, 1.00 M NaClO$_4$; T: C_{Sc} M Sc(ClO$_4$)$_3$, $C_{H(T)}$ M HClO$_4$, C_A M Na$_2$A, (1.00 − 2C_A) M NaClO$_4$. The sodium ion concentration was 0.50 M in the dipicolinate measurements. To determine the stability constants, δ_j, titrations were performed at $C_{Sc}=0$. The diglycolate system was studied using both quinhydrone and glass electrodes. Both electrodes gave the same result. The quinhydrone electrode did not function well for the malonate system and this system was therefore investigated by using a glass electrode. This electrode was also used for the dipicolinate system.

All titrations were repeated at least twice and the reproducibility of the emf was usually within 0.1 mV.

The stability constant for the copper and scandium dipicolinate systems were determined by measuring the emf of cells of the following type

−Hg,Cu	C_{Sc} M Sc(ClO$_4$)$_3$ C_{Cu} M Cu(ClO$_4$)$_2$ C_A M Na$_2$A C_H M HClO$_4$ (0.50 − 2C_A) M NaClO$_4$	0.50 M NaClO$_4$	0.01 M NaCl 0.49 M NaClO$_4$	Ag-AgCl+

The solution in the amalgam half cell was prepared as before. In order to exclude oxygen, a stream of pure nitrogen was passed through the solution both before and during the titration. The solutions S and T had the following compositions: S: C_{Sc} M $Sc(ClO_4)_3$, C_{Cu} M $Cu(ClO_4)_2$, C_H M $HClO_4$, 0.50 M $NaClO_4$; T: C_{Sc} M $Sc(ClO_4)_3$, C_{Cu} M $Cu(ClO_4)_2$, C_A M Na_2A, C_H M $HClO_4$, $(0.50 - 2C_A)$ M $NaClO_4$.

The stability constants of the copper dipicolinate system were determined in titrations with $C_{Sc} = 0$. The reproducibility of the emf values was found to be within 0.2 mV when $\bar{n}_{Cu} \leq 2$. The experimental errors were larger for $\bar{n}_{Cu} > 2$ and the reproducibility in this region was within 0.5 mV.

Calorimetric determination of enthalpy changes. An isothermal-jacket calorimeter of the type described by Gerding *et al.*[8] was used. For details of the titration procedure see Ref. 8. 100 ml of a solution S, containing the central ion, was titrated with a solution T, containing the ligand. Each titration was performed at least twice. The heat change after each addition of titrant was measured with an uncertainty of ± 0.025 cal by the use of a thermistor. The resistance change of the thermistor during the initial and final periods was determined by using a recorder instead of the galvanometer of Gerding *et al.* (Ref. 8, p. 2192). In this way a continuous record of resistance *vs.* time was obtained. The resistance *vs.* time curves were linear and the slopes of the lines were approximately the same for the initial and final periods. The change of resistance caused by the heat evolved at each titration step was taken as the difference between the ordinates of these two lines at a time chosen to be 15 sec [8] after the pipette bulb in the calorimeter had been opened.

The heat equivalent, ε_v, of the calorimeter system at the various values of v ($0 \leq v \leq 20$) was determined by electrical calibration. For solutions with $C_{Na} = 0.50$ the result may be described by the equation

$$\varepsilon_v = 2.58_0 + 0.025_8 v$$

and for solutions with $C_{Na} = 1.00$ by the equation

$$\varepsilon_v = 2.56_6 + 0.025_4 v$$

The solutions S and T had the following compositions: S: C_{Sc} M $Sc(ClO_4)_3$, C_H M $HClO_4$, 1.00 M $NaClO_4$; T: C_A M Na_2A, $(1.00 - 2C_A)$ M $NaClO_4$. The sodium ion concentration was 0.50 M in the dipicolinate measurements. The heats measured had to be corrected for the heats of dilution of the ligand solution and for the heat effects caused by the formation or dissociation of proton ligand complexes. The heats of dilution were determined by adding T to a solution S where $C_{Sc} = C_H = 0$. The heats of protonation of the ligands, needed for the calculation of the second correction, were determined in titrations with the following solutions: S: C_A M Na_2A, $(1.00 - 2C_A)$ M $NaClO_4$; T: C_H M $HClO_4$, 1.00 M $NaClO_4$. For dipicolinic acid the sodium ion concentration was 0.50 M as before. In this case the heats of dilution of the titrants were determined with $C_A = 0$ in S.

It was assumed that the heats of dilution of the scandium ion and the various complexes were small enough to neglect for our titrations.

CALCULATIONS AND RESULTS

Determination of the stability constants for the proton ligand complexes

From the emf values measured, and the known volumes of the solutions S and T, corresponding values of $\bar{n}_H$ and [H] were obtained. The stability constants, δ_j, were calculated from corresponding values of X and [H]. The various X-values were obtained by graphical evaluation of the Fronæus integral (2). For further details see Ref. 13 pp. 108—109. The constants were finally refined by the "Letagrop"-method.[15] Titrations were made at $C_A = 0.010$, 0.050, and 0.100 for diglycolic acid and at $C_A = 0.005$, 0.010, and

0.040 for dipicolinic acid. The dipicolinate titration at $C_A = 0.040$ had to be interrupted at $\bar{n}_H \approx 0.5$ because of precipitation of NaHA. Some of the experimental data are given in Table 1 and the constants obtained have been col-

Table 1. Corresponding values of v, $-\log[H]$, and $\bar{n}_H$ for the proton ligand systems.

a. The proton diglycolate system.

S: $C_A = 0.1006$, $C_H = 0.2038$, $C_{Na} = 1.00$, $v_0 = 15.00$ (ml)
T: $C_A = 0.1006$, $C_H = 0.0018$, $C_{Na} = 1.00$
v (ml), $-\log[H]$, $\bar{n}_H$: 0, 1.895, 1.900; 1.60, 2.260, 1.777; 3.60, 2.568, 1.610; 6.10, 2.806, 1.429; 9.32, 3.026, 1.248; 13.70, 3.229, 1.062; 16.70, 3.333, 0.964; 20.10, 3.431, 0.875.
S: $C_A = 0.1006$, $C_H = 0.0018$, $C_{Na} = 1.00$, $v_0 = 15.00$ (ml)
T: $C_A = 0.1006$, $C_H = 0.2038$, $C_{Na} = 1.00$
v (ml), $-\log[H]$, $\bar{n}_H$: 0, 5.480, 0.018; 0.80, 4.640, 0.120; 1.70, 4.332, 0.222; 2.60, 4.145, 0.314; 3.80, 3.969, 0.423; 6.40, 3.715, 0.617; 10.00, 3.485, 0.818; 15.00, 3.269, 1.017; 18.30, 3.166, 1.115.
S: $C_A = 0.01006$, $C_H = 0.02038$, $C_{Na} = 1.00$, $v_0 = 15.00$ (ml)
T: $C_A = 0.01006$, $C_H = 0.00018$, $C_{Na} = 1.00$
v (ml), $-\log[H]$, $\bar{n}_H$: 0, 2.461, 1.678; 1.60, 2.612, 1.585; 2.60, 2.694, 1.524; 3.60, 2.770, 1.465; 4.80, 2.857, 1.397; 6.10, 2.936, 1.326; 7.60, 3.022, 1.252; 9.30, 3.107, 1.176; 11.40, 3.196, 1.091; 13.70, 3.283, 1.012; 15.00, 3.327, 0.971; 16.70, 3.379, 0.922; 20.10, 3.470, 0.838.
S: $C_A = 0.01006$, $C_H = 0.00014$, $C_{Na} = 1.00$, $v_0 = 15.00$ (ml)
T: $C_A = 0.01006$, $C_H = 0.02034$, $C_{Na} = 1.00$
v (ml), $-\log[H]$, $\bar{n}_H$: 0, 5.715, 0.014; 0.80, 4.681, 0.114; 1.70, 4.359, 0.214; 2.60, 4.170, 0.304; 3.80, 3.994, 0.410; 5.00, 3.862, 0.502; 6.40, 3.742, 0.596; 8.10, 3.627, 0.695; 10.00, 3.523, 0.787; 12.30, 3.421, 0.881; 15.00, 3.325, 0.971.

b. The proton dipicolinate system.

S: $C_A = 0.01000$, $C_H = 0.02000$, $C_{Na} = 0.50$, $v_0 = 20.00$ (ml)
T: $C_A = 0.01000$, $C_H = 0.50$
v (ml), $-\log[H]$, $\bar{n}_H$: 0, 2.201, 1.370; 1.88, 2.292, 1.318; 5.95, 2.502, 1.226; 9.96, 2.718, 1.143; 16.00, 3.114, 1.034; 20.99, 3.487, 0.943; 24.78, 3.714, 0.874; 30.80, 3.959, 0.776; 36.78, 4.124, 0.697; 42.79, 4.266, 0.632; 50.79, 4.393, 0.561; 58.79, 4.488, 0.504; 66.79, 4.569, 0.458.
S: $C_A = 0.01000$, $C_{Na} = 0.50$, $v_0 = 20.00$ (ml)
T: $C_A = 0.01000$, $C_H = 0.02000$, $C_{Na} = 0.50$
v (ml), $-\log[H]$, $\bar{n}_H$: 0.48, 5.292, 0.047; 1.01, 5.517, 0.096; 1.50, 5.316, 0.139; 2.00, 5.167, 0.181; 3.00, 4.958, 0.260; 4.05, 4.794, 0.335; 5.01, 4.674, 0.399; 6.02, 4.564, 0.460; 8.02, 4.376, 0.568; 10.00, 4.209, 0.661; 12.05, 4.042, 0.743; 15.00, 3.808, 0.842; 20.01, 3.414, 0.962; 25.00, 3.111, 1.034.
S: $C_A = 0.00500$, $C_H = 0.01000$, $C_{Na} = 0.50$, $v_0 = 20.00$ (ml)
T: $C_A = 0.00500$, $C_{Na} = 0.50$
v (ml), $-\log[H]$, $\bar{n}_H$: 0, 2.439, 1.273; 1.99, 2.530, 1.229; 5.02, 2.669, 1.170; 9.02, 2.867, 1.107; 13.02, 3.085, 1.047; 17.01, 3.330, 0.987; 21.00, 3.582, 0.923; 24.95, 3.786, 0.857.
S: $C_A = 0.00500$, $C_{Na} = 0.50$, $v_0 = 20.00$ (ml)
T: $C_A = 0.00500$, $C_H = 0.01000$, $C_{Na} = 0.50$
v (ml), $-\log[H]$, $\bar{n}_H$: 1.06, 5.522, 0.095; 1.51, 5.340, 0.140; 2.51, 5.073, 0.221; 3.50, 4.894, 0.295; 4.50, 4.753, 0.364; 6.00, 4.586, 0.456; 7.52, 4.441, 0.539; 9.51, 4.275, 0.634; 12.02, 4.077, 0.734; 15.00, 3.856, 0.829; 20.00, 3.516, 0.939; 24.95, 3.266, 1.002.

lected in Table 2. The values of the stability constants for the proton malonate system have been determined by Dellien and Grenthe.[14] In no instance was any significant variation of δ_j with C_A found, *i.e.* only two protonated complexes HA^- and H_2A, are formed and their stability constants do not vary in

Table 2. The stability constants δ_j for the proton diglycolate, dipicolinate, and malonate systems, calculated with the "Letagrop" procedure. All errors are equal to three standard deviations.

	δ_1 (M^{-1})	δ_2 (M^{-2})
Diglycolate	$(5.70 \pm 0.06) \times 10^3$	$(2.84 \pm 0.03) \times 10^6$
Dipicolinate	$(3.16 \pm 0.03) \times 10^4$	$(3.17 \pm 0.12) \times 10^6$
Malonate	$(1.16 \pm 0.01) \times 10^5$	$(4.49 \pm 0.03) \times 10^7$

the concentration range investigated. It was assumed that the δ_j-values remained the same in solutions where $C_{Sc} \neq 0$.

Determination of the stability constants for the metal complexes

The scandium malonate system. Corresponding values of $\bar{n}$ and [A] were obtained from the [H] measured, the known volumes of the solutions S and T and the known values of δ_j by the following equations

$$\bar{n} = \frac{C_A - [A](1 + \delta_1[H] + \delta_2[H]^2)}{C_{Sc}} \quad (7)$$

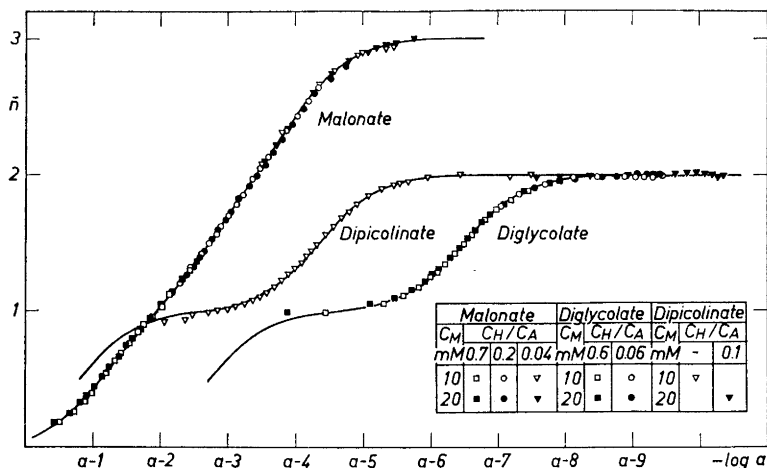$$[A] = \frac{C_H - [H]}{\delta_1[H] + 2\delta_2[H]^2} \quad (8)$$

Malonate			Diglycolate		Dipicolinate	
C_M	C_H/C_A		C_M	C_H/C_A	C_M	C_H/C_A
mM	0.7	0.2	0.04	mM	0.6	0.06	mM	-	0.1
10	□	○	▽	10	□	○	10	▽	
20	■	●	▼	20	■	●	20		▼

Fig. 1. The complex formation functions for the scandium malonate, diglycolate, and dipicolinate systems. The values of a are, respectively, 6, 10, and 11. The full-drawn curves have been computed from the experimentally determined stability constants.

Table 3. Corresponding values of v, $-\log[H]$, $\bar{n}$, and $-\log[A]$ for the scandium malonate system. The volume of the solution S is 15.00 ml in all the titrations.

S: $C_{Sc}=0.01998$, $C_H=0.00426$, $C_{Na}=1.00$
T: $C_{Sc}=0.01998$, $C_A=0.08055$, $C_H=0.05481$, $C_{Na}=1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 0.80, 2.231, 0.176, 6.601; 1.20, 2.206, 0.246, 6.374; 1.70, 2.182, 0.328, 6.215; 2.10, 2.172, 0.386, 6.113; 2.60, 2.170, 0.451, 5.992; 3.20, 2.172, 0.522, 5.878; 3.80, 2.182, 0.585, 5.769; 4.40, 2.191, 0.643, 5.684; 5.00, 2.206, 0.695, 5.595; 5.70, 2.223, 0.751, 5.507; 6.40, 2.241, 0.801, 5.424; 7.20, 2.263, 0.854, 5.337; 8.10, 2.290, 0.907, 5.244; 9.00, 2.317, 0.954, 5.157; 10.00, 2.343, 1.003, 5.077; 11.10, 2.373, 1.050, 4.990; 12.30, 2.402, 1.097, 4.909; 13.60, 2.429, 1.143, 4.834; 15.00, 2.458, 1.187, 4.759; 17.00, 2.492, 1.243, 4.671; 19.00, 2.522, 1.292, 4.595; 21.00, 2.549, 1.334, 4.529; 23.00, 2.574, 1.370, 4.469; 25.00, 2.595, 1.404, 4.420.
S: $C_{Sc}=0.01998$, $C_A=0.08055$, $C_H=0.01947$, $C_{Na}=1.00$
T: $C_{Sc}=0.01998$, $C_H=0.00426$, $C_{Na}=1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 0, 4.517, 2.801, 2.269; 1.00, 4.319, 2.712, 2.495; 2.00, 4.140, 2.600, 2.703; 3.00, 3.981, 2.485, 2.892; 4.00, 3.852, 2.371, 3.050; 5.00, 3.734, 2.266, 3.199; 6.00, 3.631, 2.168, 3.333; 7.00, 3.540, 2.079, 3.456; 8.00, 3.457, 1.997, 3.571; 9.00, 3.379, 1.923, 3.682; 10.00, 3.313, 1.853, 3.780; 11.00, 3.254, 1.789, 3.870; 12.00, 3.201, 1.729, 3.953; 13.00, 3.156, 1.672, 4.028; 14.00, 3.110, 1.620, 4.104; 15.00, 3.070, 1.571, 4.173; 16.00, 3.032, 1.525, 4.238; 17.00, 3.002, 1.480, 4.294; 18.00, 2.970, 1.439, 4.353; 19.00, 2.938, 1.401, 4.412; 20.00, 2.909, 1.365, 4.467; 21.00, 2.884, 1.330, 4.515; 22.00, 2.860, 1.297, 4.564; 23.00, 2.838, 1.266, 4.609; 24.00, 2.816, 1.236, 4.654; 25.00, 2.794, 1.209, 4.699.
S: $C_{Sc}=0.01998$, $C_A=0.1208$, $C_H=0.00435$, $C_{Na}=1.00$
T: $C_{Sc}=0.01998$, $C_H=0.00426$, $C_{Na}=1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 0, 6.178, 3.002, 1.248; 2.00, 6.058, 2.979, 1.369; 4.00, 5.930, 2.969, 1.499; 6.00, 5.788, 2.960, 1.642; 8.00, 5.629, 2.937, 1.801; 10.10, 5.424, 2.905, 2.007; 12.00, 5.216, 2.840, 2.216; 14.00, 4.958, 2.746, 2.477; 16.00, 4.714, 2.618, 2.725; 18.00, 4.511, 2.479, 2.933; 20.00, 4.327, 2.345, 3.124; 22.00, 4.167, 2.219, 3.294; 24.00, 4.021, 2.105, 3.451.
S: $C_{Sc}=0.00999$, $C_H=0.00213$, $C_{Na}=1.00$
T: $C_{Sc}=0.00999$, $C_A=0.4028$, $C_H=0.02741$, $C_{Na}=1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 0.80, 2.517, 0.180, 6.508; 1.20, 2.480, 0.254, 6.298; 1.70, 2.449, 0.338, 6.129; 2.10, 2.434, 0.397, 6.025; 3.20, 2.417, 0.537, 5.806; 4.40, 2.422, 0.658, 5.625; 5.70, 2.441, 0.764, 5.466; 7.20, 2.475, 0.861, 5.032; 9.00, 2.517, 0.955, 5.141; 11.10, 2.566, 1.041, 4.984; 13.60, 2.610, 1.129, 4.849; 17.00, 2.667, 1.217, 4.696; 21.00, 2.713, 1.302, 4.575.
S: $C_{Sc}=0.00999$, $C_A=0.04028$, $C_H=0.00974$, $C_{Na}=1.00$
T: $C_{Sc}=0.00999$, $C_H=0.00213$, $C_{Na}=1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 0, 4.603, 2.739, 2.483; 1.00, 4.456, 2.647, 2.655; 2.00, 4.307, 2.545, 2.829; 3.00, 4.177, 2.436, 2.985; 4.00, 4.047, 2.331, 3.141; 5.00, 3.932, 2.231, 3.283; 6.00, 3.830, 2.137, 3.411; 7.00, 3.732, 2.051, 3.537; 8.00, 3.649, 1.970, 3.648; 10.00, 3.509, 1.827, 3.844; 12.00, 3.401, 1.704, 4.005; 14.00, 3.310, 1.597, 4.148; 16.00, 3.232, 1.504, 4.277; 18.00, 3.166, 1.422, 4.392; 21.00, 3.087, 1.316, 4.540; 24.00, 3.017, 1.226, 4.676.
S: $C_{Sc}=0.00999$, $C_A=0.06042$, $C_H=0.00218$, $C_{Na}=1.00$
T: $C_{Sc}=0.00999$, $C_H=0.00213$, $C_{Na}=1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 0, 6.185, 2.934, 1.541; 2.00, 6.065, 2.927, 1.663; 4.00, 5.936, 2.929, 1.792; 6.00, 5.803, 2.906, 1.927; 8.00, 5.654, 2.877, 2.077; 10.00, 5.485, 2.835, 2.247; 12.00, 5.297, 2.768, 2.436; 14.00, 5.096, 2.675, 2.639; 16.00, 4.902, 2.558, 2.836; 18.00, 4.721, 2.433, 3.021; 20.00, 4.552, 2.310, 3.195; 22.00, 4.395, 2.193, 3.359; 24.00, 4.251, 2.083, 3.511.

The experimental data for the titrations are shown as plots of $\bar{n}$ *vs.* log[A] in Fig. 1 and Table 3 gives details of some of the titrations. In the [A]-region investigated, three complexes were formed and no evidence for the formation of higher complexes was found. For a given value of [A], $\bar{n}$ varies neither with

C_{Sc} nor with the buffer used. Thus, no polynuclear or acid complexes were formed in the concentration range used. Graphical evaluation of the integral (2) gave corresponding values of X and [A] from which the constants β_j were obtained. These constants were refined using the "Letagrop" method [15] and the following result was obtained:

$$\beta_1 = (7.44 \pm 0.33) \times 10^5 \quad (M^{-1})$$
$$\beta_2 = (1.33 \pm 0.06) \times 10^{10} \quad (M^{-2})$$
$$\beta_3 = (1.18 \pm 0.06) \times 10^{13} \quad (M^{-3})$$

The errors quoted above and in the following are estimated maximum errors (three standard deviations, *i.e.* a confidence interval of 99 %).

The scandium diglycolate system. For this system the concentration of free hydrogen ions is approximately the same as the total concentration C_H for values of $\bar{n} < 1$. The concentration of free ligand, [A], cannot be determined with any degree of accuracy in this range as the proton cannot compete with the metal ion for the ligand in the range where the first complex is formed. For values of $\bar{n} > 1$ the difference $C_H - [H] \neq 0$ and accurate values of [A] may be determined.

Table 4. Corresponding values of v, $-\log[H]$, $\bar{n}$, and $-\log[A]$ for the scandium diglycolate system.

S: $C_{Sc} = 0.01998$, $C_H = 0.00426$, $C_{Na} = 1.00$, $v_0 = 15.00$ (ml)
T: $C_{Sc} = 0.01998$, $C_A = 0.1006$, $C_H = 0.05658$, $C_{Na} = 1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 3.70, 1.839, 0.993, 7.125; 4.20, 1.860, 1.052, 5.915; 4.70, 1.890, 1.099, 5.544; 5.30, 1.922, 1.157, 5.293; 6.00, 1.958, 1.221, 5.086; 6.50, 1.976, 1.268, 4.985; 7.00, 1.998, 1.311, 4.885; 8.00, 2.039, 1.392, 4.718; 9.00, 2.077, 1.467, 4.577; 10.00, 2.113, 1.537, 4.457; 11.00, 2.152, 1.597, 4.339; 12.00, 2.187, 1.655, 4.235; 13.00, 2.231, 1.703, 4.119; 14.00, 2.272, 1.747, 4.015; 15.00, 2.318, 1.785, 3.915; 16.10, 2.361, 1.825, 3.800; 17.00, 2.405, 1.849, 3.701; 18.00, 2.451, 1.875, 3.600; 19.00, 2.497, 1.896, 3.501; 20.00, 2.544, 1.913, 3.402; 21.10, 2.591, 1.929, 3.304; 22.00, 2.630, 1.939, 3.226; 23.00, 2.674, 1.946, 3.139; 24.00, 2.710, 1.954, 3.068; 25.00, 2.745, 1.960, 2.999.
S: $C_{Sc} = 0.01998$, $C_H = 0.0426$, $C_{Na} = 1.00$, $v_0 = 10.00$ (ml)
T: $C_{Sc} = 0.01998$, $C_A = 0.1006$, $C_H = 0.0609$, $C_{Na} = 1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 6.00, 2.796, 1.772, 3.935; 7.00, 3.041, 1.907, 3.449; 8.00, 3.425, 1.969, 2.837; 9.00, 3.715, 1.985, 2.448; 10.00, 3.891, 1.990, 2.231; 13.00, 4.151, 2.002, 1.926; 16.00, 4.282, 2.004, 1.777; 19.00, 4.363, 2.000, 1.684; 22.00, 4.415, 2.004, 1.624; 25.00, 4.454, 2.006, 1.579.
S: $C_{Sc} = 0.00999$, $C_H = 0.00213$, $C_{Na} = 1.00$, $v_0 = 15.00$ (ml)
T: $C_{Sc} = 0.00999$, $C_A = 0.05030$, $C_H = 0.02829$, $C_{Na} = 1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 3.70, 2.143, 0.990, 6.573; 4.20, 2.154, 1.056, 5.703; 4.70, 2.167, 1.115, 5.402; 5.30, 2.192, 1.179, 5.174; 6.00, 2.206, 1.250, 4.994; 6.50, 2.221, 1.297, 4.888; 7.00, 2.236, 1.341, 4.798; 8.00, 2.267, 1.423, 4.643; 9.00, 2.297, 1.496, 4.512; 10.00, 2.329, 1.560, 4.393; 12.00, 2.392, 1.671, 4.188; 14.00, 2.463, 1.754, 3.991; 16.00, 2.539, 1.815, 3.802; 18.00, 2.610, 1.863, 3.636; 19.00, 2.645, 1.882, 3.557; 20.00, 2.683, 1.895, 3.477.
S: $C_{Sc} = 0.00999$, $C_A = 0.05030$, $C_H = 0.00304$, $C_{Na} = 1.00$, $v_0 = 15.00$ (ml)
T: $C_{Sc} = 0.00999$, $C_H = 0.00213$, $C_{Na} = 1.00$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 0, 4.724, 1.993, 1.562; 2.50, 4.621, 1.977, 1.688; 5.00, 4.511, 1.980, 1.818; 7.50, 4.395, 1.979, 1.953; 10.00, 4.260, 1.989, 2.109; 12.50, 4.138, 1.988, 2.288; 15.00, 3.915, 1.983, 2.516; 17.50, 3.656, 1.974, 2.846; 20.00, 3.352, 1.938, 3.291; 22.50, 3.131, 1.862, 3.682; 25.00, 3.005, 1.771, 3.947.

The experimental data are given in Fig. 1 and Table 4. As with the malonate system, no indication was found for the formation of acid or polynuclear complexes. The highest $\bar{n}$-value measured was two and no evidence of the formation of a third complex was found in the [A]-region investigated.

The $\bar{n}$-curve has a pronounced inflexion at $\bar{n}=1$. This means that the ratio between the two stepwise stability constants is large ($>10^3$) and that the concentration of uncomplexed scandium is negligible for $\bar{n}>1$. Only the second stepwise stability constant K_2 can thus be determined from these data. K_2 was determined by curve-fitting [13, p. 87] and the following value was obtained

$$\log K_2 = 4.49 \pm 0.02$$

The pronounced inflexion in the $\bar{n}$-curve at $\bar{n}=1$ means that the lower limit of $\log K_1$ is approximately 7.5.

The copper and scandium dipicolinate systems. The competition between copper and scandium for the ligand was used for determining the stability constants for the scandium dipicolinate system. The emf of the cell used gave values of X for the copper system.[11] The values of β_j for this system were determined from corresponding values of X and [A]. These were obtained as follows: Due to the very strong complexing of the system no values of [A], in the region where $C_A < 2C_{Cu}$, could be obtained by the ordinary extrapolation method.[11] On the other hand, [A] can here be neglected in comparison with C_A, i.e. $\bar{n} = C_A/C_{Cu}$. In the region where $C_A > 2\,C_{Cu}$, [A] could be determined from [H]-measurements. The value of [A] is given by

$$[A] = (C_A - 2C_{Cu})/(1 + \delta_1[H] + \delta_2[H]^2) \tag{9}$$

Table 5. Experimental data for the copper dipicolinate titrations.

a. Corresponding values of v and $\log X$ in the region where $C_A/C_{Cu} < 2$. The volume of the solution S is 15.00 ml.

S: $C_{Cu} = 0.02208$, $C_H = 0.003$, $C_{Na} = 0.50$
T: $C_{Cu} = 0.02208$, $C_A = 0.0900$, $C_H = 0.003$, $C_{Na} = 0.50$
v (ml), $\log X$: 0.41, 0.054; 0.82, 0.112; 1.20, 0.162; 1.66, 0.227; 2.01, 0.287; 2.53, 0.382; 3.02, 0.473; 3.50, 0.578; 4.00, 0.696; 4.51, 0.828; 5.20, 1.007; 5.90, 1.206; 6.60, 1.396; 7.30, 1.575; 8.00, 1.748; 9.00, 2.012; 10.00, 2.285; 11.00, 2.596; 12.00, 2.968; 13.01, 3.495; 14.00, 4.490.
S: $C_{Cu} = 0.01104$, $C_H = 0.003$, $C_{Na} = 0.50$
T: $C_{Cu} = 0.01104$, $C_A = 0.0600$, $C_H = 0.003$, $C_{Na} = 0.50$
v (ml), $\log X$: 0.40, 0.047; 0.84, 0.105; 1.23, 0.166; 1.62, 0.220; 2.02, 0.291; 2.51, 0.385; 3.00, 0.490; 3.50, 0.615; 4.00, 0.751; 4.49, 0.913; 5.10, 1.109; 5.73, 1.305; 6.30, 1.491; 6.90, 1.677; 7.51, 1.880; 8.20, 2.126; 8.90, 2.397; 9.60, 2.718; 10.30, 3.144; 11.00, 3.824; 11.50, 4.706.

b. Corresponding values of C_{Cu}, C_A, $\log X$, $-\log[H]$, and $-\log[A]$ in the region where $C_A/C_{Cu} > 2$.

C_{Cu}, C_A, $\log X$, $-\log[H]$, $-\log[A]$: 0.02208, 0.04781, 10.63, 4.439, 2.782; 0.02208, 0.04645, 9.49, 3.900, 3.342;[a] 0.01104, 0.02778, 9.11, 3.251, 3.540; 0.01104, 0.03913, 8.96, 2.759, 3.586; 0.01104, 0.02364, 7.92, 3.230, 4.124.

[a] Denotes upper integration limit.

Thus corresponding values of X and [A] were obtained. Graphical evaluation of the integral (2), where $(X_0, [A]_0)$ is chosen in the region $C_A > 2C_{Cu}$, then gave corresponding values of X and [A] over the whole region investigated from which values of β_j were determined. The experimental data are given in Table 5. The following values of the constants were obtained:

$$\beta_1 = (7.60 \pm 0.15) \times 10^8 \quad (M^{-1})$$
$$\beta_2 = (1.48 \pm 0.02) \times 10^{16} \quad (M^{-2})$$

These constants may be systematically in error by at most 10 % as the reproducibility of the emf-values was only within 0.5 mV in the region where $X([A]_0)$ is determined.

The stability constants for the scandium dipicolinate complexes were determined from the known stability constants of the copper complexes and the various total concentrations in the following manner. The emf of the cell measured gives $\bar{n}_{Cu}$ and [A]. Corresponding values of $\bar{n}_{Sc}$ and [A] are then obtained from the equation

$$C_A = [A] + \bar{n}_{Cu} \cdot C_{Cu} + \bar{n}_{Sc} \cdot C_{Sc} + [HA] + [H_2A] \tag{10}$$

where [A], [HA], and [H$_2$A] in this case could be neglected for $[A] < 10^{-6.5}$ For higher [A]-values the [H] of the solution was measured and, since [A] was known, [HA] and [H$_2$A] could be calculated.

The complex formation between scandium and dipicolinate was so strong that copper was not able to compete with scandium until $\bar{n}_{Sc} \approx 1$. Even in this instance a pronounced inflexion occurs in the $\bar{n}$-curve at $\bar{n} = 1$. Thus only K_2 for the scandium system could be determined since no accurate values of [A] were obtained in the region where the first complex is formed. The experimental data are given in Table 6 and Fig. 1. The $\bar{n}$-log[A] data for the

Table 6. Experimental data for the scandium dipicolinate titrations.

a. Corresponding values of v, $\log X_{Cu}$, $\bar{n}_{Sc}$, and $-\log[A]$ for the amalgam measurements.

S: $C_{Sc} = 0.01030$, $C_{Cu} = 0.01104$, $C_H = 0.005$, $C_{Na} = 0.50$, $v_0 = 15.00$ (ml)
T: $C_{Sc} = 0.01030$, $C_{Cu} = 0.01104$, $C_A = 0.0720$, $C_H = 0.005$, $C_{Na} = 0.50$
v (ml), $\log X_{Cu}$, $\bar{n}_{Sc}$, $-\log[A]$: 2.50, 0.037, 0.919, 9.9; 2 80, 0.071, 0.938, 9.6; 3.00, 0.088, 0.969, 9.5; 3.40, 0.152, 0.985, 9.3; 3.70, 0.193, 1.005, 9.16; 4.00, 0.247, 1.007, 9.02; 4.40, 0.311, 1.038, 8.89; 4.80, 0.382, 1.058, 8.755; 5.20, 0.456, 1.080, 8.635; 5.60, 0.534, 1.106, 8.525; 6.00, 0.612, 1.136, 8.425; 6.50, 0.710, 1.181, 8.310; 7.00, 0.804, 1.231, 8.205; 7.50, 0.896, 1.277, 8.110; 8.00, 0.997, 1.319, 8.010; 8.50, 1.092, 1.360, 7.915; 9.00, 1.176, 1.407, 7.840; 9.50, 1.264, 1.449, 7.770; 10.00, 1.355, 1.486, 7.690; 11.00, 1.514, 1.563, 7.560; 12.00, 1.680, 1.625, 7.435; 13.00, 1.845, 1.685, 7.320; 14.00, 2.018, 1.734, 7.205; 15.00, 2.194, 1.789, 7.095; 16.50, 2.484, 1.851, 6.920; 18.00, 2.822, 1.904, 6.720; 19.00, 3.130, 1.930, 6.540; 19.50, 3.279, 1.946, 6.455; 20.00, 3.519, 1.955, 6.325; 21.00, 4.084, 1.982, 6.040; 23.00, 5.858, 2.004, 5.154; 25.00, 7.142, 2.006, 4.512.

b. Corresponding values of v, $-\log[H]$, $\bar{n}$, and $-\log[A]$ for the [H]-measurements.

S: $C_{Sc} = 0.02014$, $C_A = 0.07084$, $C_H = 0.00791$, $C_{Na} = 0.50$, $v_0 = 20.00$ (ml)
T: $C_{Sc} = 0.02014$, $C_H = 0.01600$, $C_{Na} = 0.50$
v (ml), $-\log[H]$, $\bar{n}$, $-\log[A]$: 0, 4.975, 1.992, 1.641; 1.00, 4.867, 1.985, 1.717; 2.00, 4.755, 2.001, 1.810; 3.02, 4.633, 2.011, 1.917; 4.01, 4.500, 2.017, 2.038; 5.00, 4.348, 2.016, 2.179; 6.00, 4.162, 2.008, 2.357; 7.02, 3.891, 2.001, 2.625; 8.00, 3.480, 1.992, 3.053; 9.00, 2.990, 1.987, 3.618; 10.00, 2.659, 1.987, 4.075; 11.00, 2.446, 1.985, 4.432; 12.00, 2.282, 1.987, .826.

second step were treated as for the diglycolate system. The following value of log K_2 was obtained

$$\log K_2 = 7.66 \pm 0.01$$

The occurrence of the pronounced inflexion on the $\bar{n}$-curve at $\bar{n}=1$ implies that the lower limit of $\log K_1$ is approximately 10.7.

The titrations were interrupted at $[A]=10^{-4.5}$ and up to this $[A]$-value not more than two complexes were formed. To check whether this was true even at higher values of $[A]$, a $[H]$-investigation of the type described for the malonate system was performed, but no evidence of a third complex was found (Fig. 1, Table 6).

Determination of K_1 for the diglycolate and dipicolinate systems

It was not possible to determine values of K_1 for the diglycolate and dipicolinate systems by a potentiometric technique. Values of K_1 may be determined by a calorimetric competition method using lutetium as a competing central ion.

Table 7. Determination of K for the scandium dipicolinate and diglycolate systems.

a. Corresponding values of $-Q$, x, y, and K for the scandium dipicolinate system. K was calculated using $\Delta H_{1(Sc)} = -3.99$ kcal/mole and $\Delta H_{1(Lu)} = -2.18$ kcal/mole. The total amount of Sc was 0.496 mmole and of Lu 2.475 mmole.

$-Q$ (cal), x (mmole), y (mmole), K: 0.74, 0.181, 0.009, 160; 0.72, 0.166, 0.024, 50; 0.99, 0.239, 0.015, 160; 1.45, 0.342, 0.039, 140; 1.47, 0.355, 0.026, 240; 1.44, 0.331, 0.047, 100; 1.90, 0.434, 0.074, 230; 2.08, 0.463, 0.108, 310; 2.03, 0.427, 0.141, 100; 2.20, 0.452, 0.182, 130; 2.53, 0.478, 0.283, 210; 2.80, 0.477, 0.411, 130;

b. Corresponding values of $-Q$, x, y, and K for the scandium diglycolate system. K was calculated using $\Delta H_{1(Sc)} = -0.47$ kcal/mole and $\Delta H_{1(Lu)} = 1.29$ kcal/mole. The total amount of Sc was 0.496 mmole and of Lu 2.475 mmole.

$-Q$ (cal), x (mmole), y (mmole), K: 0.11, 0.249, 0.006, 450; 0.10, 0.241, 0.013, 180; 0.17, 0.372, 0.010, 730; 0.16, 0.366, 0.016, 430; 0.13, 0.443, 0.065, 320; 0.15, 0.453, 0.056, 460; 0.13, 0.443, 0.065, 320; 0.13, 0.443, 0.065, 320; 0.11, 0.477, 0.096, 620;

A solution, T, containing the ligand was added to a solution, S, containing lutetium and scandium and the heat evolved was measured, *cf.* Table 7. Then

$$Q = x\Delta H_{1(Sc)}{}^\circ + y\Delta H_{1(Lu)}{}^\circ \tag{11}$$

if x mole ScA and y mole LuA are formed. Moreover the added number of moles of ligand, z, is known and

$$z = x + y + [A] \cdot V \tag{12}$$

V is the total volume of solution in the calorimeter. As the complexes formed are known to be very strong, $[A]$ is neglected, and x and y can be evaluated

from (11) and (12) if the $\Delta H°$-values are known. From the known total concentrations, all quantities on the left hand side in eqn. (13) may then be calculated and, since $K_{1(Lu)}$ is known,[1-3] $K_{1(Sc)}$ can be calculated.

$$K = K_{1(Sc)}/K_{1(Lu)} = [ScA][Lu]/[LuA][Sc] \tag{13}$$

However, the scandium complexes are so much stronger than the corresponding lutetium complexes that only relatively small amounts of LuA are formed in the region where the first scandium complex is formed. Consequently the values of K_1 are impaired by fairly large errors. The values found are for the dipicolinate system

$$\log K_1 = 11.2 \pm 0.2$$

and for the diglycolate system

$$\log K_1 = 8.28 \pm 0.15$$

Determination of the heats of formation of the proton ligand complexes

The experimental data used for determining the heats of formation of the proton ligand complexes are given in Table 8. The values of [H] were calculated from the known total concentrations of the solutions and the known values of δ_j. From the values of $\sum Q_{corr}$ and [H] corresponding values

Table 8. Determination of the heats of formation for the proton ligand complexes.

a. Heats of dilution of the perchloric acid solutions.
S: 1.00 M $NaClO_4$; T: $C_H=0.603$, $C_{Na}=1.00$
v (ml), Q (cal): 1.904, 0.07; 3.808, 0.05; 5.712, 0.06; 7.618, 0.07; 9.520, 0.08.
S: 0.50 M $NaClO_4$; T: $C_H=0.535$, $C_{Na}=0.50$
v (ml), Q (cal): 1.904, 0.09; 3.808, 0.09; 5.712, 0.08; 7.618, 0.07; 9.520, 0.08.

b. Corresponding values of v, $\sum Q_{corr}$ and $-\log[H]$ for the proton malonate system.
S: $C_A=0.0503$; $C_{Na}=1.00$; T: $C_H=0.603$, $C_{Na}=1.00$
v (ml), $\sum Q_{corr}$ (cal), $-\log[H]$: 2.009, 0.58, 5.553; 4.018, 1.18, 5.097; 6.027, 1.74, 4.662; 8.036, 2.18, 3.983; 10.05, 2.02, 3.187; 12.05, 1.67, 2.752; 14.06, 1.36, 2.415; 16.07, 1.09, 2.114; 18.08, 0.98, 1.863.

c. Corresponding values of v, $\sum Q_{corr}$ and $-\log[H]$ for the proton diglycolate system.
S: $C_A=0.506$, $C_{Na}=1.00$; T: $C_H=0.603$, $C_{Na}=1.00$
v (ml), $\sum Q_{corr}$ (cal), $-\log[H]$: 1.904, 0.85, 4.319; 3.808, 1.57, 3.921; 5.712, 2.16, 3.638; 7.616, 2.57, 3.389; 9.520, 2.76, 3.146; 11.42, 2.73, 2.910; 13.33, 2.61, 2.648; 15.23, 2.40, 2.361; 17.14, 2.24, 2.061; 19.04, 2.20, 2.914.
d. Corresponding values of v, $\sum Q_{corr}$ and $-\log[H]$ for the proton dipicolinate system.
S: $C_A=0.02504$, $C_{Na}=0.50$; T: $C_H=0.535$, $C_{Na}=0.50$
v (ml), $\sum Q_{corr}$ (cal), $-\log[H]$: 1.904, 0.13; 4.668; 3.808, 0.27, 3.900; 5.712, -0.06, 2.738; 6.664, -0.37, 2.428; 7.618, -0.66, 2.228; 8.568, -0.89, 2.058; 9.520, ... precipitation.

of γ_n and [H] were obtained from which the various ΔH_j°-values were determined by a graphical method similar to that which gave β_j-values from corresponding values of X and [A]. For further details see Refs. 3 and 13. The ΔH_j°-values derived are collected in Table 9. Owing to the small heats evolved,

Table 9. The stepwise values of ΔH° for the formation of proton diglycolate, dipicolinate and malonate complexes, with their estimated errors.

Ligand	ΔH_1° (kcal·mole^{-1})	ΔH_2° (kcal·mole^{-1})
Diglycolate	0.76 ± 0.04	-0.38 ± 0.06
Dipicolinate	0.15 ± 0.01	-1.10 ± 0.06
Malonate	0.48 ± 0.01	-0.35 ± 0.01

the precision is not very high but no efforts were made to get more accurate values since these ΔH_j°-values were only used in making small corrections.
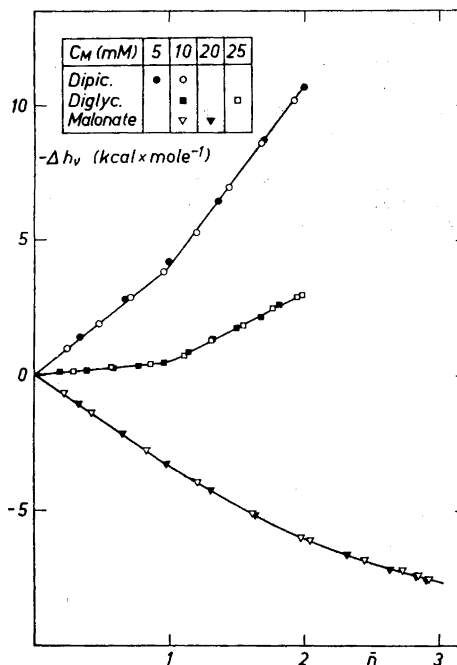

Fig. 2. The molar enthalpy change Δh_v as a function of $\bar{n}$ for the scandium malonate, diglycolate, and dipicolinate systems at different central ion concentrations.

Determination of the heats of formation for the metal complexes

The scandium malonate system. The ΔH_j°-values of this system were obtained from corresponding values of $\sum Q_{corr}$ and [A] in the same way as has been described for the proton ligand complexes. The values of [A] were calculated, as previously described, from the [H] of the solution, measured in a separate titration. From the [H] measured the amounts of HA^- and H_2A formed or dissociated during each addition were calculated, and the heats obtained were corrected by taking this into account. Corrections were also made for the heats of dilution of the ligand solution. In Fig. 2 Δh_v is plotted

Table 10. Determination of the heats of formation for the scandium malonate complexes.

a. Heats of dilution of the malonate solutions.

S: 1.00 M $NaClO_4$; T: $C_A = 0.4024$, $C_{Na} = 1.00$
v (ml), Q (cal): 2.009, 0.04; 4.018, 0.02; 6.027, 0.03; 8.036, 0.04; 10.05, 0.02.
S: 1.00 M $NaClO_4$; T: $C_A = 0.2515$, $C_{Na} = 1.00$
v (ml), Q (cal): 2.009, 0.00; 4.018, −0.01; 6.027, 0.00; 8.036, 0.00; 10.05, 0.00.

b. Corresponding values of v, $\sum Q$, $\sum Q_{corr}$ and $\bar{n}$ for the scandium malonate titrations.

S: $C_{Sc} = 0.01982$, $C_H = 0.01004$, $C_{Na} = 1.00$
T: $C_A = 0.4024$, $C_H = 0.00256$, $C_{Na} = 1.00$
v (ml), $\sum Q$ (cal), $\sum Q_{corr}$ (cal), $\bar{n}$: 2.009, 2.22, 2.15, 0.324; 4.018, 4.45, 4.30, 0.650; 6.027, 6.70, 6.45, 0.973; 8.036, 8.75, 8.39, 1.299; 10.05, 10.76, 10.26, 1.631; 12.05, 12.57, 11.97, 1.971; 14.06, 13.96, 13.27, 2.316; 16.07, 15.02, 14.27, 2.626; 18.08, 15.60, 14.80, 2.815; 20.09, 15.88, 15.04, 2.889.
S: $C_{Sc} = 0.00991$, $C_H = 0.00502$, $C_{Na} = 1.00$
T: $C_A = 0.2515$, $C_H = 0.00160$, $C_{Na} = 1.00$
v (ml), $\sum Q$ (cal), $\sum Q_{corr}$ (cal), $\bar{n}$: 2.009, 1.42, 1.39, 0.423; 4.018, 2.76, 2.69, 0.823; 6.027, 4.02, 3.90, 1.206; 8.036, 5.26, 5.08, 1.613; 10.05, 6.28, 6.06, 2.035; 12.05, 7.01, 6.77, 2.435; 14.06, 7.43, 7.18, 2.718; 16.07, 7.62, 7.37, 2.834; 18.08, 7.72, 7.46, 2.900; 20.09, 7.78, 7.52, 2.917.

vs. $\bar{n}$. The values of $\bar{n}$ were calculated from the [H] of the solution. For a given value of $\bar{n}$ no variation of Δh_v with C_{Sc} was found. This once more indicates that no polynuclear complexes were formed. The experimental data for some of the titrations are given in Table 10 and the values of ΔH_j° refined by a least-squares procedure are tabulated in Table 11.

The scandium diglycolate system. As the two steps of the complex formation are well separated the values of ΔH_j° are obtained by plotting Δh_v *vs.* $\bar{n}$ (Fig. 2). ΔH_1° and $(\Delta H_1^\circ + \Delta H_2^\circ)$ are then given by the ordinates at $\bar{n} = 1$ and $\bar{n} = 2$, respectively. For $C_A < C_{Sc}$, $\bar{n}$ equals to C_A/C_{Sc} as [A], [HA], and [H_2A] are negligible relative to C_A. In the region where $C_A > C_{Sc}$, $\bar{n}$ was calculated from the [H] of the solution and corrections in Q_{corr} were made for the heats arising from the formation or dissociation of HA^- and H_2A. The heats of dilution of the ligand solutions used were found to be zero within the experimental errors. No effects due to the formation of polynuclear complexes were detected (Fig. 2). Corresponding values of v, $\sum Q$, $\sum Q_{corr}$ and $\bar{n}$ for some of the titrations

Table 11. The stepwise values of ΔG_j°, ΔH_j°, and ΔS_j° for the formation of scandium dipicolinate, diglycolate, and malonate complexes, with their estimated errors. The data refer to a temperature of 25.00°C and a medium of the total sodium ion concentration 0.50 M for the dipicolinate and 1.00 M for the diglycolate and malonate systems.

Ligand	$-\Delta G_1^\circ$ (kcal·mole^{-1})	$-\Delta H_1^\circ$ (kcal·mole^{-1})	ΔS_1° (e.u.)
Dipicolinate	15.3 ± 0.3	3.99 ± 0.02	37.9 ± 1.1
Diglycolate	11.3 ± 0.2	0.47 ± 0.01	36.3 ± 0.7
Malonate	8.01 ± 0.03	− 3.41 ± 0.02	38.3 ± 0.2
	$-\Delta G_2^\circ$ (kcal·mole^{-1})	$-\Delta H_2^\circ$ (kcal·mole^{-1})	ΔS_2° (e.u.)
Dipicolinate	10.42 ± 0.01	6.73 ± 0.03	12.3 ± 0.1
Diglycolate	6.12 ± 0.03	2.55 ± 0.02	12.0 ± 0.2
Malonate	5.80 ± 0.05	− 2.93 ± 0.03	29.3 ± 0.3
	$-\Delta G_3^\circ$ (kcal·mole^{-1})	$-\Delta H_3^\circ$ (kcal·mole^{-1})	ΔS_3° (e.u.)
Malonate	3.95 ± 0.02	− 1.46 ± 0.04	18.1 ± 0.2

Table 12. Corresponding values of v, $\sum Q$, $\sum Q_{corr}$, and $\bar{n}$ for the scandium diglycolate titrations.

S: $C_{Sc} = 0.02478$, $C_H = 0.01255$, $C_{Na} = 1.00$
T: $C_A = 0.3544$, $C_H = 0.00188$, $C_{Na} = 1.00$
v (ml), $-\sum Q$ (cal), $-\sum Q_{corr}$ (cal), $\bar{n}$: 2.009, 0.33, 0.33, 0.287; 4.018, 0.684, 0.684, 0.575; 6.027, 1.01, 1.01, 0.862; 8.036, 1.73, 1.78, 1.106; 10.05, 3.00, 3.13, 1.315; 12.05, 4.41, 4.62, 1.547; 14.06, 5.81, 6.11, 1.770; 16.07, 6.69, 7.17, 1.946; 18.08, 6.64, 7.37, 1.989; 20.09, 6.60, 7.42, 1.987.
S: $C_{Sc} = 0.00999$, $C_H = 0.00213$, $C_{Na} = 1.00$
T: $C_A = 0.1013$, $C_{Na} = 1.00$
v (ml), $-\sum Q$ (cal), $-\sum Q_{corr}$ (cal), $\bar{n}$: 1.904, 0.10, 0.10, 0.191; 3.808, 0.19, 0.19, 0.386; 5.712, 0.26, 0.26, 0.582; 7.616, 0.34, 0.34, 0.772; 9.520, 0.47, 0.47, 0.963; 11.42, 0.86, 0.87, 1.142; 13.33, 1.31, 1.33, 1.319; 15.23, 1.76, 1.79, 1.492; 17.14, 2.18, 2.22, 1.679; 19.04, 2.56, 2.62, 1.813.

are given in Table 12. The least-squares refined values of ΔH_j° obtained are found in Table 11.

The scandium dipicolinate system. Even for this system, values of ΔH_j° could be obtained from a plot of Δh_v *vs.* $\bar{n}$ (Fig. 2). In the region where $C_A < 2 C_{Sc}$, $[A] \ll C_A$ and thus $\bar{n} = C_A / C_{Sc}$. As no appreciable amounts of HA$^-$ or H$_2$A are formed in this region the only correction made in Q_{corr} is that for the heat of dilution. For $C_A > 2 C_{Sc}$, corrections are also made for the heats arising from the formation or dissociation of HA$^-$ and H$_2$A. Similarily to the systems previously described, no effects due to the formation of polynuclear complexes were found (Fig. 2). Table 13 gives the heats of dilution and the

Table 13. Determination of the heats of formation for the scandium dipicolinate complexes.

a. Heats of dilution of the dipicolinate solutions.

S: 0.50 M $NaClO_4$; T: $C_A = 0.1263$, $C_{Na} = 0.50$
v (ml), Q (cal): 1.904, 0.01; 3.808, 0.02; 5.712, 0.02; 7.616, 0.03; 9.520, 0.03.
S: 0.50 M $NaClO_4$; T: $C_A = 0.0840$, $C_{Na} = 0.50$
v (ml), Q (cal): 2.009, 0.01; 4.018, 0.00; 6.027, 0.02; 8.036, 0.02; 10.05, 0.01.

b. Corresponding values of v, $\sum Q_{corr}$ and C_A/C_{Sc} for the scandium dipicolinate titrations.

S: $C_{Sc} = 0.00999$, $C_H = 0.0082$, $C_{Na} = 0.50$
T: $C_A = 0.1263$, $C_H = 0.0025$, $C_{Na} = 0.50$
v (ml), $-\sum Q_{corr}$ (cal), C_A/C_{Sc}: 1.904, 0.97, 0.241; 3.808, 1.91, 0.482; 5.712, 2.87, 0.722;
7.616, 3.83, 0.963; 9.520, 5.29, 1.204; 11.42, 6.95, 1.444; 13.33, 8.58, 1.685; 15.23, 10.18,
1.926; 17.14, 10.66, 2.166; 19.04, 10.63, 2.407.
S: $C_{Sc} = 0.004955$, $C_H = 0.00254$, $C_{Na} = 0.50$
T: $C_A = 0.0840$, $C_{Na} = 0.50$
v (ml), $-\sum Q_{corr}$ (cal), C_A/C_{Sc}: 2.009, 0.70, 0.341; 4.018, 1.39, 0.681; 6.027, 2.085, 1.022;
8.036, 3.18, 1.362; 10.05, 4.31, 1.703; 12.05, 5.29, 2.043.

corresponding values of v and $\sum Q_{corr}$ for some of the titrations. The least-squares refined values of ΔH_j° obtained are given in Table 11.

CONCLUSIONS

The experimental values for the changes in free energy, enthalpy, and entropy for the various complex formation reactions are given in Table 11. A comparison of these values for the diglycolate and dipicolinate complexes with the corresponding values for the tervalent lanthanoids may be summarised as follows.

1. The over-all stability constants for the scandium complexes are larger than the corresponding constants for the lanthanoid complexes. This arises from the increase in stability of the first complex; the second stepwise stability constant for the scandium complexes is smaller than the corresponding constants for the heavier lanthanoids. The ratio K_1/K_2, of the first and second stepwise constants for the scandium complexes is sufficiently large ($\approx 10^4$) for a pronounced inflexion to appear at $\bar{n} = 1$ in the $\bar{n}$ vs. log[A] curves.

2. The maximum number of ligands bonded is two, *i.e.* the coordination number for scandium(III) is at least six. An increasing difficulty in forming a third complex has already been noted for the lanthanoid series in which the constant, K_3, gradually decreases with decreasing ionic radius of the central ion from dysprosium to lutetium. The decrease in ionic radius from lutetium to scandium is clearly large enough to entirely prevent the formation of a third complex.

3. In a previous publication,[5] some general trends in the variation of ΔH_j° and ΔS_j°, with respect to the ionic radius of the central ion, were pointed out. The experimental results in this investigation show that scandium falls into the same general pattern, at least as far as ΔH_1° and ΔS_1° are concerned.

Table 11 shows that the ligand malonate has a different behaviour to that of diglycolate and dipicolinate. The maximum number of malonate ligands bonded to scandium is three, *i.e.* the coordination number for scandium(III) is still at least six. There is no difficulty in forming the third complex. This complex seems to be formed more easily than the second if judged from the ratios K_1/K_2 and K_2/K_3 ($K_1/K_2=42$, $K_2/K_3=20$). The formation of malonate complexes is endothermic and their existence is due entirely to the favourable entropy change. Free energy, enthalpy, and entropy data are not available yet for lanthanoid malonate complexes. Measurements of this type are in progress at this institute and a further discussion of malonate complexes will be postponed until these investigations are completed.

The different behaviour of diglycolate and dipicolinate complexes as compared to malonate complexes is probably related to the fact that the first two ligands are tridentate whereas the last one is bidentate. A tridentate ligand can be expected to have less "freedom" to form coordinated bonds than a bidentate ligand, *i.e.* the complexes formed by the tridentate ligands are more susceptible to changes in the ionic radius of the central ion.

REFERENCES

1. Grenthe, I. *J. Am. Chem. Soc.* **83** (1961) 360.
2. Grenthe, I. and Tobiasson, I. *Acta Chem. Scand.* **17** (1963) 2101.
3. Grenthe, I. *Acta Chem. Scand.* **17** (1963) 2487.
4. Grenthe, I. *Acta Chem. Scand.* **18** (1964) 283.
5. Grenthe, I. *Acta Chem. Scand.* **18** (1964) 293.
6. Grenthe, I., Gårdhammar, G. and Rundcrantz, E. *Acta Chem. Scand.* **23** (1969) 93.
7. Wyckoff, R. W. G. *Crystal Structures*, Interscience, New York, London, Sydney, Vol. **2**, p. 5.
8. Gerding, P., Leden, I. and Sunner, S. *Acta Chem. Scand.* **17** (1963) 2190.
9. Wünsch, L. *Collection Czech. Chem. Commun.* **20** (1955) 1107.
10. Biedermann, G., Kilpatric, M., Pokras, L. and Sillén, L. G. *Acta Chem. Scand.* **10** (1956) 1327.
11. Fronæus, S. *Komplexsystem hos koppar*, (Diss.), Lund 1948.
12. Brown, A. S. *J. Am. Chem. Soc.* **56** (1934) 646.
13. Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants*, McGraw, New York, Toronto, London 1961.
14. Dellien, I. and Grenthe, I. *To be published*.
15. Ingri, N. and Sillén, L. G. *Arkiv Kemi* **23** (1964) 97.