ACTA CHEMICA SCANDINAVICA 27 (1973) 2431–2440

Thermodynamic Properties of Rare Earth Complexes

XVIII. Free Energy, Enthalpy, and Entropy Changes for the Formation of Some Lanthanoid Thiodiacetate and Hydrogen Thiodiacetate Complexes

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The changes in free energy, enthalpy and entropy for the formation of Ce, Pr, Sm, Tb, Er, and Yb thiodiacetate and hydrogen thiodiacetate complexes with the compositions MA, MA_2, MHA and MHA_2 have been determined. The changes in free energy were calculated from stability constants, obtained from a potentiometric determination of the concentration of free hydrogen ion, using a glass electrode. The enthalpy values were measured calorimetrically. The measurements were performed at 25.0°C in an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M.

The possible formation of a complex MA_3 has been investigated in the praseodymium and ytterbium systems, using 4.00 M $Na(ClO_4)$ as ionic medium.

The changes in thermodynamic functions such as ΔG_j°, ΔH_j°, and ΔS_j° for the formation of lanthanoid(III)-complexes usually do not follow the monotonic dependence on the size of the metal ion as is suggested by simple electrostatic models of bonding. This non-monotonic size dependence is not a consequence of differences in electron configuration, as all the tervalent rare earth ions have a "noble gas" like configuration of the outer electron shells. Hence, one should try to base models which describe the observed size specificity in the complexation reactions on factors such as the size of the central ion, the geometrical requirements of the ligand, and the coordination of solvent molecules to the species participating in the complex formation reactions.

The coordinated donor atoms in the ligands may be described as forming a cavity, the size of which depends on the size of the central ion and the way in which the donor atoms are interconnected in the ligand. In general, one must expect that a coordinated ligand can not be arranged as freely as the solvent molecules in the coordination shell. Hence, the cavities formed by the coordinated donor atoms in multidentate ligands cannot contract to the same extent as the cavities formed by the coordinated solvent molecules as the size of the metal ion decreases. The resulting differences in the geometry of the coordination spheres will give rise to a size specificity in the complexation reactions.

In previous parts of this series we have reported thermodynamic data for complexation reactions in aqueous solution between rare earths and the terdentate ligands 2,6-pyridinedicarboxylate (=dipicolinate[1]), iminodiacetate,[2] and oxydiacetate.[3] They all form stable chelates with a maximum of three ligands coordinated in each case, presumably giving rise to ninecoordinated complexes in solution. The variations through the rare earth series of the thermodynamic quantities are also very similar, *e.g.* the pronounced difficulty for the third complex to be formed for the central ions with the smallest ionic radius. The observed similarities are probably due to a similar coordination geometry for the three ligands, as judged from the structures of solids containing the complexes.[4,5]

We have extended the previous investigations to include the terdentate ligand thiodiacetate, which contains a sulphur atom as the third donor atom. As the rare earths are typical a-acceptors and thus have a much smaller affinity to sulphur than to nitrogen and oxygen, a substantial decrease in stability is expected for the thiodiacetate complexes as compared to those with nitrogen and oxygen donors.

The radius of the sulphur atom is about 30 % larger than the radii of nitrogen and oxygen. Sulphur atoms in the equatorial plane of a tricapped trigonal prism, which is the most common coordination polyhedron in solid rare earth complexes are, because of their size, expected to be closer to one another than the equatorial atoms in the dipicolinate, iminodiacetate and oxydiacetate complexes. Thus, purely geometrical constraints might give an additional decrease in stability for the higher thiodiacetate complexes.

In systems containing polyprotic acids and their conjugate bases, the possibility of complex formation with all these various ligands must be kept in mind. This will lead to an increased difficulty in the interpretation of the experimental data, especially when the concentration of free ligand can not be measured directly. Acid complexes have been found only for the iminodiacetate systems,[2] a fact that undoubtedly is due to the high basicity of iminodiacetate as compared to the other ligands. Thiodiacetate has very nearly the same base strength as oxydiacetate. On the other hand, the expected decrease in stability of the thiodiacetate complexes ought to increase the possibility for acid complexes to appear in noticeable amounts.

Because of the similarity in geometry of oxydiacetate, iminodiacetate, dipicolinate, and thiodiacetate, it is expected that they will interact in a similar way with a given lanthanoid ion. The pronounced similarities in the variations of the ΔH_j° and ΔS_j° values through the lanthanoid series for the oxydiacetate, iminodiacetate, and dipicolinate complexes can thus be expected to include also the thiodiacetate complexes.

This study of lanthanoid thiodiacetates has been undertaken mainly in order to obtain quantitative information about the coordinating ability of various donors in rare earth complexes of similar geometry. Measurements have been performed in solutions with a high concentration of hydrogen thiodiacetate ion in order to get information concerning the formation of acid complexes. The changes in $\Delta G_j°$, $\Delta H_j°$ and $\Delta S_j°$ have been determined for six lanthanoid ions, *viz.* Ce^{3+}, Pr^{3+}, Sm^{3+}, Tb^{3+}, Er^{3+}, and Yb^{3+}, which should give sufficient information on the variation pattern of these properties across the lanthanoid series. The stability constants have been calculated from potentiometric determinations of the concentration of free hydrogen ion by means of a glass electrode. The various enthalpies of complexation have been determined calorimetrically. Most data refer to a temperature of 25.0°C and an aqueous sodium perchlorate medium with the sodium ion concentration equal to 1.00 M. However, in order to obtain information on the possible formation of a third complex, accurate experimental data at high ligand concentrations are needed. This is not easy, as changes in the composition of the medium will cause changes in the activity coefficients of the reacting species and/or the appearance of diffusion potentials in the emf measurements. In order to minimize these effects and get as accurate emf-data as possible, even at high concentrations of the ligand, stability constants for the praseodymium and ytterbium systems have also been measured in 4.00 M $NaClO_4$.

NOTATIONS AND CALCULATIONS

The notations have been defined previously.[2,8]

The stability constants and enthalpy values have been calculated from the experimentally determined values of (v/ml, E/mV) and (v/ml, Q_{corr}/J), respectively, by the least-squares procedures "Etiter" and "Kalle" in the "Letagrop" series.[6,7] The proton thiodiacetate system has also been treated with standard graphical procedures.

EXPERIMENTAL

Chemicals used. A stock solution of cerium perchlorate was prepared by dissolving cerium(III) nitrate (BDH, 99 %) in perchloric acid, precipitating the cerium as carbonate and redissolving the precipitate in perchloric acid. The other metal perchlorate solutions were prepared and analyzed as described before.[8] Thiodiacetic acid (Schuchard, 98 %) was purified with active charcoal and recrystallized twice from water. The purity was checked by alkalimetric titration and the formula weight was found to be 150.4 (calc. 150.1).

The various buffers were obtained by mixing the appropriate amounts of solutions of thiodiacetic acid and sodium hydroxide. The sodium ion concentration was adjusted to 1.00 M (or 4.00 M, respectively) by addition of sodium perchlorate solution.

Potentiometric measurements. The equipment and experimental procedure in the potentiometric measurements were the same as described earlier.[8]

The protonation constants of the thiodiacetate ion were determined in solutions with $C_M = 0$ and with different, constant values of C_A. In 1 M $Na(ClO_4)$, these values of C_A were equal to 20 mM, 40 mM, and 100 mM, respectively. For the corresponding measurements in 4 M $Na(ClO_4)$, the C_A-values were 50 mM, 100 mM, and 200 mM, respectively.

About six titration series have been made on each of the lanthanoid thiodiacetate systems, using solutions with different compositions. A wide concentration range with respect to thiodiacetate and hydrogen thiodiacetate ion must be covered in order to get solutions containing measurable amounts of the various complexes. The ratio C_H/C_A in the different solutions varied from 2 to 1/10, and the total metal ion concentration varied from 8 mM to 35 mM. Table 1 shows the compositions of the solutions used for the measurements on the terbium system.

Table 1. Experimental results of the potentiometric measurements on the terbium system. The results are given as v/ml, E/mV, $\bar{n}_{\mathrm{H}}$, $(\bar{n}_{\mathrm{H,\,calc}}-\bar{n}_{\mathrm{H,\,exp}})\times 10^3$. The sodium ion concentration is 1.00 M in all solutions. Approximately one half of the experimental data are given.

Series 1. S: $C_{\mathrm{H}}=0.00068$ M, $C_{\mathrm{M}}=0.03184$ M, $C_{\mathrm{A}}=0$; T: $C_{\mathrm{H}}=0.06098$ M, $C_{\mathrm{M}}=0$, $C_{\mathrm{A}}=0.1906$ M; $V_0=20.00$ ml, $E_0=361.1$ mV.

0.900, 147.9, *0.369*, 1.21; 1.400, 145.3, *0.353*, 2.53; 2.500, 141.1, *0.340*, 5.42; 3.900, 136.4, *0.333*, 6.80; 5.300, 132.1, *0.330*, 6.80; 6.800, 127.9, *0.328*, 4.65; 8.500, 123.9, *0.327*, 1.97; 10.60, 120.1, *0.325*, −0.18; 13.60, 116.0, 0.324, −4.47; 17.00, 112.9, *0.323*, −7.46; 22.00, 109.8, *0.323*, −11.88; 28.00, 107.6, *0.322*, −14.32; 35.00, 105.9, *0.322*, −16.89;

Series 2. S: $C_{\mathrm{H}}=0.05061$ M, $C_{\mathrm{M}}=0.01990$ M, $C_{\mathrm{A}}=0.02509$ M; T: $C_{\mathrm{H}}=0.00064$ M, $C_{\mathrm{M}}=0.01990$ M, $C_{\mathrm{A}}=0.05018$ M; $V_0=20.00$ ml, $E_0=361.5$ mV.

0.0, 226.1, *1.812*, −1.18; 0.400, 221.2, *1.774*, −1.19; 0.800, 216.6, *1.732*, −1.77; 1.300, 211.5, *1.677*, −1.22; 1.800, 206.9, *1.622*, −2.70; 2.500, 201.5, *1.545*, −2.63; 3.200, 196.9, *1.473*, −3.28; 4.100, 191.9, *1.388*, −4.16; 5.200, 186.8, *1.295*, −5.02; 6.500, 181.8, *1.198*, −5.09; 8.000, 117.0, *1.103*, −3.90; 10.00, 171.6, *0.997*, −3.12; 12.10, 166.8, *0.905*, −2.64; 14.60, 161.9, *0.816*, −2.43; 17.70, 156.8, *0.727*, −0.83; 21.20, 151.8, *0.648*, −1.03; 25.40, 146.8, *0.573*, 0.48; 30.20, 141.9, *0.507*, 1.14; 36.00, 136.9, *0.445*, 1.88;

Series 3. S: $C_{\mathrm{H}}=0.1405$ M, $C_{\mathrm{M}}=0.01990$ M, $C_{\mathrm{A}}=0.07005$ M; T: $C_{\mathrm{H}}=0.00064$ M, $C_{\mathrm{M}}=0.01990$ M, $C_{\mathrm{A}}=0.05018$ M; $V_0=20.00$ ml, $E_0=361.5$ mV.

0.0, 234.7, 1.865, 0.02; 0.600, 229.3, 1.834, 0.46; 1.150, 224.7, 1.803, 0.77; 1.800, 219.8, 1.764, 1.30; 2.550, 214.8, 1.717, 1.44; 3.400, 209.9, 1.664, 1.27; 4.400, 205.0, 1.603, 1.09; 5.600, 200.0, 0.07; 7.100, 194.9, 1.455, 0.82; 8.800, 189.9, 1.373, −1.58; 10.90, 184.9, 1.284, −0.95; 13.40, 179.9, 1.191, −0.49; 16.40, 174.8, 1.095, −1.11; 20.00, 169.6, 0.999, −2.60; 24.00, 164.9, 0.910, −0.27; 29.00, 159.8, 0.819, −0.02; 35.20, 154.5, 0.729, 0.52;

Table 2. Experimental results of the calorimetric measurements on the terbium system. Corresponding values of v/ml, $Q_{\mathrm{corr,\,exp}}$/J and $(Q_{\mathrm{corr,\,calc}}-Q_{\mathrm{corr,\,exp}})\times 10^3$/J are given. The sodium ion concentration is 1.00 M in all solutions.

Series 1. S: $C_{\mathrm{H}}=0.000417$ M, $C_{\mathrm{M}}=0.02023$ M, $C_{\mathrm{A}}=0$; T: $C_{\mathrm{H}}=0.05870$ M, $C_{\mathrm{M}}=0$, $C_{\mathrm{A}}=0.2660$ M; $V_0=79.98$ ml.

1.000, 3.008, 50; 3.000, 5.886, 16; 5.000, 5.112, 12; 7.000, 4.326, −46; 9.000, 3.518, −42; 11.00, 2.824, −46; 13.00, 2.255, −42; 15.00, 1.585, 181; 17.00, 1.426, −8; 19.00, 1.100, 55;

Series 2. S: $C_{\mathrm{H}}=0.000417$ M, $C_{\mathrm{M}}=0.02023$ M, $C_{\mathrm{A}}=0$; T: $C_{\mathrm{H}}=0.05870$ M, $C_{\mathrm{M}}=0$, $C_{\mathrm{A}}=0.2660$ M; $V_0=79.98$ ml.

2.000, 6.054, 46; 4.000, 5.497, 29; 6.000, 4.723, −12; 8.000, 3.945, −76; 10.00, 5.150, −34; 12.00, 2.531, −55; 14.00, 1.995, −20; 16.00, 1.548, 29; 18.00, 1.246, 29; 20.00, 1.033, 12;

Series 3. S: $C_{\mathrm{H}}=0.2441$ M, $C_{\mathrm{M}}=0$, $C_{\mathrm{A}}=0.2374$ M; T: $C_{\mathrm{H}}=0.000417$ M, $C_{\mathrm{M}}=0.02023$ M, $C_{\mathrm{A}}=0$, $V_0=79.98$ ml.

1.000, 0.397, 16; 3.000, 0.790, 29; 5.000, 0.811, 4; 7.000, 0.803, 8; 9.000, 0.820, −16; 11.00, 0.774, 20; 13.00, 0.782, 4; 15.00, 0.799, −16; 17.00, 0.765, 8; 19.00, 0.761, 8;

Series 4. S: $C_{\mathrm{H}}=0.2441$ M, $C_{\mathrm{M}}=0$, $C_{\mathrm{A}}=0.2374$ M; T: $C_{\mathrm{H}}=0.000417$ M, $C_{\mathrm{M}}=0.02023$ M, $C_{\mathrm{A}}=0$; $V_0=79.98$ ml.

2.000, 0.832, −8; 4.000, 0.811, 8; 6.000, 0.824, −12; 8.000, 0.815, −8; 10.00, 0.757, 41; 12.00, 0.807, −12; 14.00, 0.794, −8; 16.00, 0.753, 25; 18.00, 0.728, 41; 20.00, 0.728, 37;

Series 5. S: $C_{\mathrm{H}}=0.000417$ M, $C_{\mathrm{M}}=0.02023$ M, $C_{\mathrm{A}}=0$; T: $C_{\mathrm{H}}=0.2441$ M, $C_{\mathrm{M}}=0$, $C_{\mathrm{A}}=0.2374$ M; $V_0=79.98$ ml.

3.000, 3.631, −25; 5.000, 2.096, 0; 7.000, 2.058, −134; 9.000, 1.962, −205; 11.00, 1.594, 4; 13.00, 1.489, −29; 15.00, 1.347, −20; 17.00, 1.171, 29; 19.00, 1.117, −25;

Series 6. S: $C_{\mathrm{H}}=0.000417$ M, $C_{\mathrm{M}}=0.02023$ M, $C_{\mathrm{A}}=0$; T: $C_{\mathrm{H}}=0.2441$ M, $C_{\mathrm{M}}=0$, $C_{\mathrm{A}}=0.2374$ M; $V_0=79.98$ ml.

2.000, 2.464, 71; 4.000, 2.196, −4; 6.000, 1.987, 25; 8.000, 1.849, −12; 10.00, 1.707, −33; 12.00, 1.460, 64; 14.00, 1.384, 4; 16.00, 1.280, −16; 18.00, 1.167, −20;

For the measurements in 4 M $Na(ClO_4)$, only one buffer solution with the ratio C_H/C_A equal to 1/5 was used, and three titration series were made for each system. A precipitate with the composition $M_2A_3.nH_2O$ is formed during the titration, but it was dissolved if T solution was added in excess at once.

Calorimetric measurements. The measurements were performed as titrations in the same way as described earlier.[9]

The heats of protonation of thiodiacetate ion were determined by titrating a disodium thiodiacetate solution with perchloric acid.

In order to determine the enthalpies of formation of the various lanthanoid-thiodiacetate complexes, titration series have been made with solutions of the following types:

Metal perchlorate solutions were titrated with thiodiacetate buffers with the ratio C_H/C_A equal to 1 or 1/4. In the third type of titration, a hydrogen thiodiacetate solution was titrated with a metal perchlorate solution.

The different solutions used for the measurements on the terbium system are given in Table 2. Most of the titrations were repeated once. The heats of dilution of the various T solutions were determined in separate experiments and were found to be negligible.

RESULTS

Determination of the stability constants

Measurements in 1 M Na(ClO₄). A least-squares treatment of $(\bar{n}_H, h)$-data gave the following values of the two protonation constants of the thiodiacetate ion.

$$\beta_{0,1,1} = (9.84 \pm 0.10) \times 10^3 \ \mathrm{M}^{-1}$$
$$\beta_{0,2,1} = (1.34 \pm 0.01) \times 10^7 \ \mathrm{M}^{-2}$$

(The errors given above and in the following are equal to three standard deviations). The standard deviation in $\bar{n}_H$ was equal to 2.7×10^{-3}, and 102 experimental points were used in the calculation.

The constants vary somewhat with C_A; $\beta_{0,1,1}$ thus increased with approx. 1 % as C_A is increased from 20 mM to 40 mM. This variation might be caused by an uncompensated liquid junction potential.

Some experimental values of $\bar{n}^*$ *vs.* $-\log(a^*/\mathrm{M})$ for the praseodymium thiodiacetate system are shown in Fig. 1 (a). The fact that different curves are obtained in titrations with different values of the ratio C_H/C_A, clearly indicates that complexes of the composition $M_pH_qA_r$ with $q > 0$ are formed.

The curves obtained at C_M equal to 19 mM and 35 mM are very nearly the same, indicating that polynuclear species are not formed in appreciable amounts. Since the highest value of $\bar{n}^*$ is 1.5, complexes with at least two ligands per metal ion must be formed, but no conclusions can be drawn about the existence of a third complex.

It is not possible in these systems to determine directly from experimental data the stoichiometry of the complexes formed; neither can standard graphical procedures be used. Instead, the results of using different "probable" models have been calculated.

In the first model, which was based on the results presented in Fig. 1 (a) the following assumptions were made:

i. Two binary complexes with the compositions MA and MA_2 are formed.
ii. One acid complex, *viz.* MHA, is formed.
iii. Polynuclear species are not formed.

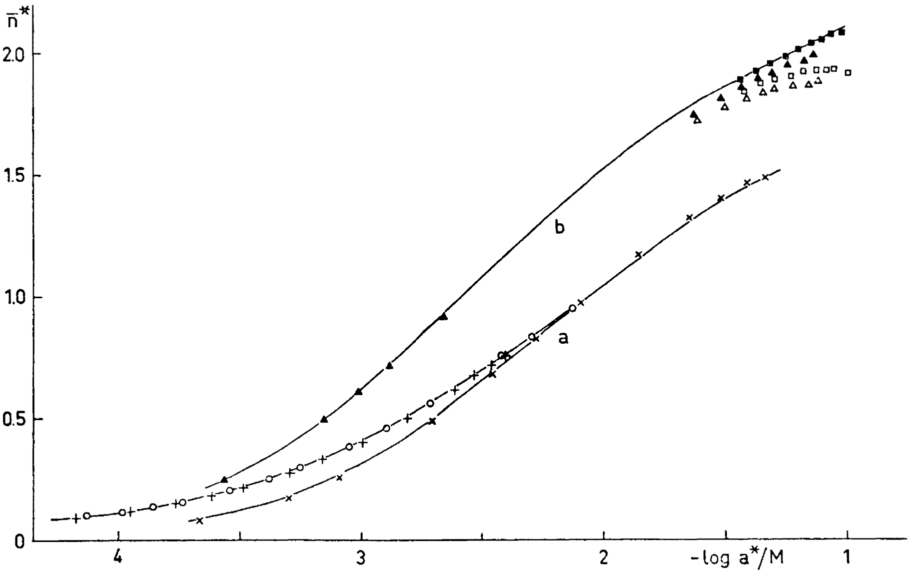

Fig. 1. Experimental $\bar{n}^*$ *vs.* $-\log (a^*/\mathrm{M})$ values for the praseodymium thiodiacetate system. *a.* Results from the measurements in 1 M $\mathrm{Na(ClO_4)}$. The curves have been calculated with the constants given in Table 3. *b.* Results from the measurements in 4 M $\mathrm{Na(ClO_4)}$. The curve is calculated with the constants given in Table 5. Values of $\bar{n}^*$ and $-\log (a^*/\mathrm{M})$ have been calculated for two titration series with different values of the protonation constant $\beta_{0,1,1}$; *viz.*

Series 1 ($V_0 = 10$ ml) $\beta_{0,1,1} = 3.93 \times 10^4/\mathrm{M}$ (■), $\beta_{0,1,1} = 3.74 \times 10^4/\mathrm{M}$ (□)
Series 2 ($V_0 = 20$ ml) $\beta_{0,1,1} = 3.84 \times 10^4/\mathrm{M}$ (▲), $\beta_{0,1,1} = 3.66 \times 10^4/\mathrm{M}$ (△)

		Solution S			Solution T		
		$\frac{C_\mathrm{H}}{\mathrm{mM}}$	$\frac{C_\mathrm{M}}{\mathrm{mM}}$	$\frac{C_\mathrm{A}}{\mathrm{mM}}$	$\frac{C_\mathrm{H}}{\mathrm{mM}}$	$\frac{C_\mathrm{M}}{\mathrm{mM}}$	$\frac{C_\mathrm{A}}{\mathrm{mM}}$
	○	122	19	60	1	19	60
a.	+	122	35	60	2	35	60
	×	0.7	15	0	42	15	181
b.	△ □	2	42	0	57	21	277

The calculated stability constants were positive and the standard deviation in $C_\mathrm{H}/C_\mathrm{A}$ was equal to 7.75×10^{-3}. (The figures refer to the terbium system).

There is no reason to include the complex $\mathrm{MA_3}$ in the calculations, but the possible presence of other acid complexes, *viz.* $\mathrm{MHA_2}$ or $\mathrm{MH_2A_2}$, has been investigated. The results are:

$\beta_{1,1,2} = (1.98 \pm 0.36) \times 10^7\ \mathrm{M}^{-3}$; *sig* $C_\mathrm{H}/C_\mathrm{A} = 4.48 \times 10^{-3}$
$\beta_{1,2,2} = (2.3 \pm 0.8) \times 10^9\ \mathrm{M}^{-4}$; *sig* $C_\mathrm{H}/C_\mathrm{A} = 6.90 \times 10^{-3}$

From these values of the stability constants, it is found that $\alpha_{1,1,2}$ amounts to 0.05 – 0.10 in some solutions, while $\alpha_{1,2,2}$ is always less than 0.01 in the solutions studied.

The possible presence of binuclear complexes M_2A and M_2HA has also been tested. These species did not improve the over-all description of the experimental data, *i.e.* the standard deviation in C_H/C_A was not lowered and the corresponding stability constants were zero or negative.

Thus, it can be concluded that the species MH_2A_2, M_2A, and M_2HA are not present in any significant amounts, if at all, in the solutions studied.

From the experimental data, stability constants for the formation of the complexes MA, MA_2, MHA, and MHA_2 have been calculated. The stability constants with their estimated errors are given in Table 3. Some of the experimental data for the terbium system are given in Table 1.

Table 3. Stability constants for the lanthanoid thiodiacetate systems studied. The errors are equal to three standard deviations.

Metal ion	Number of points	sig C_H/C_A	$\beta_{1,0,1} \times 10^{-2}$ M	$\beta_{1,0,2} \times 10^{-4}$ M^2	$\beta_{1,1,1} \times 10^{-5}$ M^2	$\beta_{1,1,2} \times 10^{-7}$ M^3
Ce	92	6.08×10^{-3}	4.53 ± 0.11	3.07 ± 0.22	2.30 ± 0.24	4.6 ± 1.2
Pr	140	5.08×10^{-3}	5.55 ± 0.17	2.43 ± 0.17	2.81 ± 0.21	4.4 ± 0.9
Sm	169	4.56×10^{-3}	8.01 ± 0.31	4.80 ± 0.24	3.91 ± 0.23	6.6 ± 1.3
Tb	110	4.48×10^{-3}	3.30 ± 0.06	1.33 ± 0.06	1.61 ± 0.11	1.98 ± 0.36
Er	120	4.07×10^{-3}	2.30 ± 0.030	0.704 ± 0.030	1.38 ± 0.07	1.61 ± 0.22
Yb	120	5.56×10^{-3}	2.30 ± 0.037	0.576 ± 0.038	1.25 ± 0.10	1.87 ± 0.30

It is assumed that the values of the protonation constants remain the same when $C_M \neq 0$ as when $C_M = 0$. This assumption was tested for the terbium system. When the protonation constants were varied with the other constants, the standard deviation in C_H/C_A was lowered from 4.48×10^{-3} to 4.01×10^{-3}, but the constants calculated in this way agreed, within the limits of error, with those given in Table 3. It can be concluded that any systematic variation of the protonation constants with C_M and C_A is less than the error limits given.

Measurements in 4 M Na(ClO$_4$). The protonation constants of the ligand must be accurately known if reliable values of $\bar{n}$ and a are to be obtained.

Table 4. The protonation constants of thiodiacetate ion in 4.00 M Na(ClO$_4$), calculated for each experimental C_A-value separately.

C_A mM	Number of points	$\beta_{0,1,1} \times 10^{-4}$ M	$\beta_{0,2,1} \times 10^{-8}$ M^2	sig (C_H/C_A)
50	69	3.66 ± 0.014	1.664 ± 0.010	1.37×10^{-3}
100	76	3.74 ± 0.012	1.668 ± 0.006	0.99×10^{-3}
200	77	3.95 ± 0.011	1.784 ± 0.006	1.02×10^{-3}

Table 4 shows the protonation constants, calculated for each experimental C_A-value separately. The increase in $\beta_{0,1,1}$ with C_A must be taken into account in the calculation of the stability constants.

For each of the praseodymium and ytterbium systems, about 30 experimental points were determined. If the presence of acid complexes is neglected in the calculations, the calculated values of the concentration of free ligand, a, and the ligand number, $\bar{n}$, are incorrect and will be denoted a^* and $\bar{n}^*$, respectively (*cf.* Ref. 8). From these ($\bar{n}^*$, a^*)-values "stability constants", β_j^*, are obtained, which are smaller than the true constants. However, the ratio $\beta_j^{*2}/(\beta_{j+1}^*\beta_{j-1}^*)$ should give a good estimate of the ratio of the stepwise stability constants, K_j/K_{j+1}. Hence, we have estimated the magnitude of the ratio K_2/K_3 from the experimental ($\bar{n}^*$, a^*)-values. For each titration series, two sets of ($\bar{n}^*$, a^*)-values have been calculated, using two different values of $\beta_{0,1,1}$. These values correspond to the smallest and largest value of C_A, respectively, which were used during the titration in the region where $\bar{n}^*$ is greater than 1.6. From the "upper limit" of ($\bar{n}^*$, a^*)-values thus obtained, the lower limit of the ratio K_2/K_3 is estimated. For the praseodymium system, experimental values of ($\bar{n}^*$, $-\log a^*/\mathrm{M}$) are shown in Fig. 1 (b), together with the $\bar{n}^*$ *vs.* $-\log (a^*/\mathrm{M})$ curve from which the lower limit of K_2/K_3 has been estimated. The ytterbium system was treated in a similar way. Table 5 gives the results and a comparison with the values obtained in 1 M Na(ClO$_4$).

Table 5. Stability constants for the formation of the non-acid complexes MA_j and the ratios of the stepwise stability constants, determined in 1 M (Na(ClO$_4$) and 4 M Na(ClO$_4$), respectively.

Metal	Medium: 1.00 M Na(ClO$_4$)			Medium: 4.00 M Na(ClO$_4$)				
ion	$\beta_{1,0,1}$ M	$\beta_{1,0,2}$ M^2	K_1/K_2	$\beta^*_{1,0,1}$ M	$\beta^*_{1,0,2}$ M^2	$\beta^*_{1,0,3}$ M^3	K_1^*/K_2^*	K_2^*/K_3^*
Pr	5.55×10^2	2.43×10^4	12.7	1.10×10^3	1.4×10^5	3×10^5	8.7	60
Yb	2.296×10^2	5.76×10^3	9.2	7.0×10^3	5.4×10^4	8×10^4	9.1	51

A "Letagrop" calculation with the acid complexes included gave the same value of K_2/K_3 as the procedure described above.

Determination of the enthalpy values

The following values for the heats of protonation of the thiodiacetate ion were obtained:

$$\Delta H^\circ_{0,1,1} = (1.82 \pm 0.11) \text{ kJ mol}^{-1}$$
$$\Delta H^\circ_{0,2,1} = (1.36 \pm 0.15) \text{ kJ mol}^{-1}$$

The standard deviation in Q_{corr} was 0.10 J and 19 experimental points were measured.

The changes in free energy and entropy for the formation of the proton-thiodiacetate complexes at 25.0°C are:

$\Delta G^\circ_{0,1,1} = (-22.79 \pm 0.02)\text{kJ mol}^{-1}$
$\Delta G^\circ_{0,2,1} = (-40.68 \pm 0.02)\text{kJ mol}^{-1}$
$\Delta S^\circ_{0,1,1} = (82.5 \pm 0.4)\text{ J K}^{-1}\text{ mol}^{-1}$
$\Delta S^\circ_{0,2,1} = (140.9 \pm 0.6)\text{ J K}^{-1}\text{ mol}^{-1}$

The heats of formation of the various rare earth thiodiacetate complexes, calculated with the least-squares procedure, are given in Table 6. The standard deviations in the individual measurements, *sig* Q_{corr}, are of the magnitude expected from the precision of the calorimetric equipment.

Table 6. The overall values of ΔH°, ΔG°, and ΔS° for the lanhtanoid thiodiacetate systems studied. The enthalpy values are tabulated with their estimated maximum errors, equal to three standard deviations. The standard deviation *sig* Q_{corr} in the measured Q_{corr} values and the number of experimental points in the calorimetric titrations are also given. The ΔH° and ΔG°-values have been divided with kJ mol^{-1}, the ΔS°-values with J K^{-1} mol^{-1}.

	Ce	Pr	Sm	Tb	Er	Yb
$\Delta H^\circ_{1,0,1}$	12.80 ± 0.29	12.16 ± 0.45	11.38 ± 0.12	17.20 ± 0.39	20.96 ± 0.33	22.38 ± 0.18
$\Delta G^\circ_{1,0,1}$	−15.15	−15.65	−16.57	−14.39	−13.47	−13.47
$\Delta S^\circ_{1,0,1}$	93.7	93.3	93.7	105.9	115.5	120.1
$\Delta H^\circ_{1,0,2}$	20.29 ± 0.45	19.7 ± 1.1	20.63 ± 0.24	26.3 ± 0.8	33.1 ± 0.8	36.1 ± 0.5
$\Delta G^\circ_{1,0,2}$	−25.61	−25.03	−26.69	−23.56	−21.97	−21.46
$\Delta S^\circ_{1,0,2}$	154	150	159	167	185	193
$\Delta H^\circ_{1,1,1}$	8.5 ± 1.3	6.4 ± 2.6	5.4 ± 0.6	12.9 ± 2.6	15.3 ± 2.3	14.7 ± 1.1
$\Delta G^\circ_{1,1,1}$	−30.59	−31.09	−31.92	−29.71	−29.33	−29.08
$\Delta S^\circ_{1,1,1}$	131	126	125	143	150	147
$\Delta H^\circ_{1,1,2}$	15.7 ± 2.5	16 ± 5	14.5 ± 1.5	20 ± 6	25.2 ± 3.8	26.6 ± 1.6
$\Delta G^\circ_{1,1,2}$	−43.7	−43.6	−44.6	−41.6	−41.1	−41.5
$\Delta S^\circ_{1,1,2}$	200	200	198	207	222	228
sig Q_{corr}/J	0.045	0.082	0.023	0.066	0.053	0.027
Number of points	58	57	48	58	57	59

DISCUSSION

The stability constants for the lanthanoid thiodiacetate complexes are considerably smaller than those for the corresponding oxydiacetate,[3] dipicolinate,[1] or iminodiacetate[2] complexes. In the oxydiacetate complexes, two five-membered chelate rings are formed, which makes these complexes stronger than the corresponding oxalate complexes. The thiodiacetate complexes are even weaker than those formed with the bidentate malonate ion.[8] One can thus safely conclude that sulphur is a much poorer donor than oxygen in this case.

For the oxydiacetates and dipicolinates there is an increased difficulty for the third complex to be formed as the ionic radius of the lanthanoid decreases, as judged from the variation of the ratio K_2/K_3 of the stepwise stability constants. This ratio increases from 30 for the light lanthanoids to more than 100 for ytterbium and lutetium. Scandium does not form any third complex at all with these ligands. A comparison with the thiodiacetates is made difficult by the experimental problems in determining the stability constant of a third complex. However, the values given above show that the ratio K_2/K_3 is larger than 60 for the thiodiacetates, *i.e.* it is indeed difficult for the third complex to be formed. The values of the ratio K_1/K_2 are about 10, which shows that there is no problem in forming the second complex. This ratio has also very nearly the same value as for the corresponding oxydiacetates. These findings indicate that the larger radius of the sulphur atom makes the formation of a third thiodiacetate complex difficult even for the lanthanoid ions with the largest ionic radii. The magnitude of the stepwise stability constant K_3 is small. This indicates that the ligand in the third complex, if this complex is formed at all, is bound only to one carboxylate group.

The stability constants for the complexation with the protonated ligand, *i.e.* $M+HA \rightleftharpoons MHA$, are in the range $12-40$ M^{-1} for the thiodiacetates, which is of the same order of magnitude as for the malonates.[8] For the hydrogen malonates, the strength of the acid MHA increases when the metal ion becomes smaller. This was described as due to an increased electrostatic repulsion between the central ion and the bonded proton when the size of the metal ion decreased. A similar result is not found for the hydrogen thiodiacetates, for which pK_a for MHA is roughly constant through the rare earth series. The larger distance between the carboxylate groups in the thiodiacetate ion as compared with the malonate ion might be an explanation for this finding.

The low stability of the thiodiacetates is mainly an enthalpy effect, whereas the entropy term is of the same order of magnitude as for the oxydiacetates. The variation pattern of the function $\Delta H_1°$ *vs.* Z and $\Delta S_1°$ *vs.* Z are very similar for the thiodiacetates, oxydiacetates,[10] dipicolinates,[10] and iminodiacetates.[2] It is reasonable to assume that these geometrically similar dicarboxylate ligands cause approximately the same changes in the hydration shell of a given metal ion, at least on the formation of the first complex. This will roughly account for the similarities in the entropy changes.

Acknowledgement. This work has been sponsored by grants from the *Swedish Natural Research Council* and *Kungl. Fysiografiska Sällskapet* in Lund.

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Received March 7, 1973.