electronegativity effects cancel, at least to a first approximation. By this treatment Ψ_{65} and Ψ_{45} in IV are 59 and 61°, respectively, so demonstrating that the $CH_2 - CH_2$ fragment adjacent to the sulfoxide group is the more puckered. The ring is also marginally more puckered than V in this region ($\Psi = 58°$). The latter value, which is 5° lower than that in 2-phenyl-1,3-dithiane, we earlier interpreted in terms of flattening due to the axial 2-methyl group and/or the presence of twist forms.[11] It seems likely that similar effects occur in IV also.

Experimental, trans-2-t-Butyl-cis-2-methyl-1,3-dithiane 1-oxide IV was prepared as described in Ref. 2.

The NMR spectrum was recorded of a 10 % solution in $CDCl_3$ using a 100 MHz Varian HA-100 spectrometer operating at 35°. Line positions were taken by averaging data from four 100 Hz sweepwidth spectra, calibrated at every 10 Hz. Spectral analysis was performed using a local version of the LAOCN3 program and carried out on a UNIVAC 1110 computer. Graphical presentation of data, Fig. 1, was obtained using a CALCOMP plotter.

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Stability Constants for Scandium Thiodiacetate Complexes

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Thermodynamic data such as $\Delta G_j°$, $\Delta H_j°$, and $\Delta S_j°$ for complex formation reactions in aqueous solution between lanthanoid(III) ions and carboxylate ligands show that these thermodynamic properties are greatly affected by the geometrical requirements of the ligand and the size of the metal ion. As scandium(III) has a similar electron configuration as the lanthanoids but is considerably smaller (the radii of the lanthanoid ions are in the range 1.06 − 0.85 Å, while that of Sc^{3+} is 0.73 Å [1]), data on scandium complexes should give additional information on the effects of a variation of the metal ion radius upon the thermodynamic characteristics of complex formation.

The earlier measurements on some lanthanoid thiodiacetate complexes [2] have here been extended to the scandium thiodiacetate system. The main reasons for this investigation are summarized below:

i. For the scandium complexes, the ratio between the consecutive formation constants, K_1/K_2, is low for the bidentate ligands malonate [3] and oxalate [4] (≈ 40), but quite high ($\approx 10^4$) for terdentate ligands such as oxydiacetate [3] and dipicolinate.[3] The lanthanoids are typical hard acids which ought to form poor bonds with sulfur donors. The results obtained from the lanthanoid thiodiacetate systems confirms this expectation, *i.e.* the ligand seems to be effectively bidentate.[2] A determination of K_1/K_2 for the scandium thiodiacetate complexes will indicate how the ligand is bonded.

ii. The stability of acid complexes as MHA^{2+} also gives information on the bonding in and the geometry of the complexes. Thus, acid complexes are not formed when the lanthanoid ion and the ligand form five-membered chelate rings, as in the oxalates [5] and oxydiacetates,[6] or when the coordinating groups are close to each other due to a rigid ligand geometry, as in the maleates.[7] The effectively bidentate ligands malonate and thiodiacetate form weaker chelate complexes,[8,2] and acid complexes are thus formed in appreciable amounts in these systems. The variation pattern of pK_a (MHA^{2+}) *versus* the lanthanoid ion radius can be qualitatively described with simple electrostatic arguments.

This communication reports a determination of the composition and stability constants for scandium thiodiacetate complexes. The measurements have been designed to make it possible to decide if any scandium hydrogen thiodiacetate complex is formed. A potentiometric

standard method has been used, viz. the deter-mination of the concentration of free hydrogen ion by means of a glass electrode. The measure-ments were performed at 25.0 °C in an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M.

Notations, calculations and experimental. Thiodiacetic acid, $S(CH_2COOH)_2$, is denoted H_2A, the other notations have been defined earlier.[8] The stability constants have been calculated from the experimentally determined E-values by the least squares procedure "Letagrop Etiter".

Scandium oxide (99.9 %) was obtained from Johnson Matthey Chem. Co. The other chemicals used were the same as described earlier.[2,8]

The equipment and experimental procedure in the potentiometric measurements were the same as used earlier. Six titration series were made, giving 76 experimental values of v/ml and E/mV. The titrator solution (T) had the composition $C_H = 63.6$ mM, $C_A = 230.9$ mM, and $C_{Sc} = 0$. The various titrand solutions (S)

Table 1. Experimental results for the scandium thiodiacetate system. The results are given as v/ml, E/mV, $\bar{n}_H$, $(\bar{n}_{H,calc} - \bar{n}_{H,exp}) \times 10^3$. Two of the six titration series are given. The sodium ion concentration is 1.00 M in all solutions.

Series 1. S: $C_H = 0.05050$ M, $C_{Sc} = 0.01860$ M, $C_A = 0$;
　　T: $C_H = 0.06360$ M, $C_{Sc} = 0$, $C_A = 0.2309$ M;
　　$V_0 = 20.00$ ml, $E_0 = -631.1$ mV

0.50, -713.8, 1.923, 1.0; 1.00, -720.9, 1.891, 9.5; 1.50, -729.7, 1.855, 5.4; 2.00, -740.1, 1.778, 15.0; 2.50, -752.0, 1.673, 12.9; 3.00, -764.4, 1.548, -4.7; 3.50, -775.6, 1.420, -11.7; 4.00, -785.7, 1.306, -6.8; 4.50, -795.3, 1.208, -0.7; 5.00, -803.7, 1.124, 9.5; 5.50, -811.3, 1.053, 11.8; 6.00, -817.7, 0.991, 12.2; 6.50, -823.3, 0.938, 8.6; 7.00, -828.2, 0.893, 3.2; 7.50, -832.6, 0.852, -3.8; 8.00, -836.3, 0.817, -7.5; 9.00, -842.6, 0.758, -14.4; 10.0, -847.9, 0.710, -22.0;

Series 2. S: $C_H = 0.0058$ M, $C_{Sc} = 0.01970$ M, $C_A = 0$;
　　T: $C_H = 0.06360$ M, $C_{Sc} = 0$, $C_A = 0.2309$ M;
　　$V_0 = 20.00$ ml, $E_0 = -631.6$ mV

0.20, -773.8, 1.061, 8.8; 0.30, -778.0, 0.968, 8.0; 0.40, -781.6, 0.888, 9.2; 0.50, -784.8, 0.824, 7.1; 0.70, -790.3, 0.727, 0.8; 0.90, -794.9, 0.659, -1.7; 1.10, -799.1, 0.610, -4.8; 1.30, -803.0, 0.572, -4.8; 1.60, -808.6, 0.530, 1.0; 1.90, -814.4, 0.499, 9.1; 2.30, -822.2, 0.469, 27.4;

had $C_{Sc} = 10$ mM or 20 mM, and C_H varied between 3 mM and 50 mM.

The titrations had to be interrupted at $\bar{n}^* \approx 1.3$, due to the formation of a precipitate of the approximate composition $ScOHA(H_2O)_{0.5}$.

Results. Some of the experimental (v/ml, E/mV) data are given in Table 1. From these values the corresponding ($\bar{n}^*, a^*$) values were calculated. Different $\bar{n}^*(a^*)$ curves were ob-tained in solutions with different values of the hydrogen ion concentration, cf. Fig. 1 in Ref. 2. As the extent of hydrolysis is small in the solutions used, it is reasonable to explain this finding by the formation of acid complexes. The highest $\bar{n}^*$ value is 1.3; thus it is probable that at most two thiodiacetate ions are coordi-nated to the scandium ion in the concentration range investigated. The formation of the solid phase prevents measurements at higher free ligand concentrations. Hence no reliable esti-mate of $\beta_{1,0,3}$ can be obtained.

The hydrolysis of the scandium ion was accounted for by using stability constants for the species $ScOH^{2+}$ and $Sc_2(OH)_2^{4+}$ from Biedermann et al.[9] in the calculations. It was assumed that thiodiacetate complexes of the composition ScA^+, ScA_2^-, and $ScHA^{2+}$ were formed, and a least squares refinement by Letagrop Etiter gave the following values:

$$\beta_{1,0,1} = (8.60 \pm 0.15) \times 10^3 \text{ M}^{-1}$$
$$\beta_{1,0,2} = (5.5 \pm 1.1) \times 10^5 \text{M}^{-2}$$
$$\beta_{1,1,1} = (1.46 \pm 0.12) \times 10^6 \text{M}^{-2}$$

(The uncertainties are equal to 3σ, where σ denotes the standard deviation). The standard deviation in the error-carrying variable C_H/C_A was equal to 9.8×10^{-3}. The accuracy of the data is lower than for the lanthanoid systems. Due to this, and the scarcity of data at high concentration of free ligand, the uncertainty in $\beta_{1,0,2}$ is rather high. It is also not possible to detect the presence of the species MHA_2, which is formed in the lanthanoid thiodiacetate and malonate systems.

The stability of the higher lanthanoid thio-diacetate complexes has been discussed earlier in some detail,[2] and it seems safe to conclude from this discussion that the formation of the complex ScA_3^{3-} can be neglected in the con-centration range investigated here.

The concentration of scandium hydroxo complexes amounts at most to 0.5 % of C_{Sc} and to 4 % of C_H. There is no indication of any complex formation between hydrolysed scan-dium ions and the thiodiacetate ion in the pH range studied. If the hydrolysis of the scandium ion is neglected, the standard devia-tion in C_H/C_A rises to 12×10^{-3}.

Discussion. It has been inferred earlier from thermodynamic measurements that sulfur is a poor donor to rare earth ions.[10,11] This conclusion is validated for scandium by the results ob-tained here.

The increase in stability for the scandium thiodiacetate complex as compared to the ytterbium complex is smaller than the corresponding increase in stability found with the ligands malonate, oxydiacetate, and dipicolinate. It might be that the gain in the standard Gibbs free energy due to the electrostatic effects of substituting a lanthanoid ion with the smaller scandium ion is partially counteracted by a distortion of the thiodiacetate ion, brought about by the coordination of the carboxylate groups.

For the scandium thiodiacetate system, K_2 has the value 65 M^{-1}, while K_2 is 2×10^4 M^{-1} for the bidentate ligand malonate and is still larger for the terdentate ligands oxydiacetate and dipicolinate. The ratio K_1/K_2 is 130 for scandium thiodiacetate, which is slightly larger than found for the malonate and oxalate complexes, but much smaller than the values found for the terdentate ligands. The magnitude of the K_1 value indicates that an eight-membered chelate ring is formed in the monothiodiacetate complex. It is suggested from the values of K_2 and K_1/K_2 that the ligand in the second complex to some extent is bonded *via* one carboxylate group only. However, definite conclusions cannot be drawn until structural data on scandium thiodiacetate complexes are available.

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