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Thermodynamics of Metal Complex Formation in Aqueous Solution. VI. Equilibrium and Enthalpy Measurements on the Zinc and Cadmium Selenocyanate Systems

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The stability constants and the enthalpy changes accompanying the formation of zinc and cadmium selenocyanate complexes have been determined by potentiometric and calorimetric measurements. From the enthalpy changes measured, and the free energy changes computed from the stability constants, the entropy changes have been calculated. All data refer to 25.0 °C and an aqueous sodium perchlorate medium of ionic strength 1.00 M.

Of the two selenocyanate systems investigated that of cadmium is the strongest one. In the systems studied most of the species are formed in exothermic reactions having entropy terms counteracting the complex formation.

Complexes of ligands coordinating *via* selenium have hitherto received relatively little attention, mainly due to experimental difficulties. Measurements have been performed with organic selenium ligands also containing sulfonate or carboxylate groups in order to make them water-soluble.[1,2] Also selenium semicarbazides have been employed.[3] The environment of the selenium atom may differ considerably between these various ligands and hence also its donor properties. Generally, the ligands have also other potential donor atoms competing with the selenium. This may obscure the interpretation of the results and thus limit the possibilities to study the donor properties of selenium.

The selenocyanate ion, $SeCN^-$, is certainly among the simplest selenium donors and a few complexes of this ligand have also been studied. Unfortunately $SeCN^-$ is not very stable in aqueous solution. Solutions of alkali selenocyanates start to decompose as the pH becomes $\lesssim 5$.[4] In the presence of transition metal ions the disintegration starts at even higher values of pH, the value depending both on the metal ion present and the concentrations used. On the other hand, most transition metal ions are perceptibly hydrolyzed already at pH = 5. It is therefore difficult, or even impossible, to investigate their selenocyanate complexes in aqueous solution.

The selenocyanate ion is a homologue to the thiocyanate ion. Metals can be linked to selenocyanate either through the selenium atom or through the nitrogen atom while coordination to thiocyanate may occur either *via* sulfur or *via* nitrogen. From a comparison of the thermodynamics for the formation of thiocyanate and selenocyanate complexes, it should be possible to draw conclusions about the nature of the bonds formed in various complex systems.

The thiocyanate complexes of the divalent zinc group ions Zn^{2+}, Cd^{2+}, and Hg^{2+} have been studied previously.[5,6] Of these ions, Zn^{2+} and Cd^{2+} are not appreciably hydrolyzed for pH < 5.[8,9] A complete study of their selenocyanate complexes is therefore feasible and will be described in this paper. As to Hg^{2+}, its rather strongly acidic properties [7] prevents the formation of stable selenocyanate complexes except at quite high ligand concentrations where the hydrolysis is sufficiently suppressed. This is in fact achieved only when the final, *i.e.* the fourth complex is the predominating one as will be discussed in Part VIII of this series.

The stability constants were determined from potentiometric measurements and the enthalpy

Table 1. Comparison of reported values of stability constants for the zinc and cadmium selenocyanate systems. The measurements refer to KNO_3 media.

Metal		Zn^{2+}	Cd^{2+}		
Ref		10	10	11	12
Temp/°C		30	30	25	20
I/M		2.0	2.0	0.8	1.5
	$j=1$	5.8	20		22
	2	10	100		182
β_j/M^{-j}	3		440		1000 [a]
	4		1000	4000	1800
	5				8000

[a] The authors gave $\beta_3 = 10\,000$ M^{-3}. According to the graphs in the paper β_3 should rather be 1 000 M^{-3}.

changes, ΔH°_j, were measured calorimetrically. From the stability constants the free energy changes were computed. Finally, the entropy changes, ΔS°_j, were obtained from the relation

$$\Delta G^\circ_j = \Delta H^\circ_j - T\Delta S^\circ_j \qquad (1)$$

Previously, a polarographic study of the zinc and cadmium selenocyanate systems has been performed by Humffray *et al.*,[10] Table 1. By the same method Toropova[11] determined β_4 of the cadmium selenocyanate system. From a potentiometric investigation Golub and Andreichenko[12] found five mononuclear cadmium selenocyanate complexes. No determination of the enthalpy changes for the formation of zinc and cadmium selenocyanate complexes seems to have been published so far.

Like the previous investigations in this series, the present one was performed at 25.0 °C and in an aqueous medium of unit ionic strength, with sodium perchlorate as supplementary electrolyte.

CALCULATIONS

The notation is the same as in previous papers of this series.[13,14]

Calculation of stability constants from potentiometric measurements of the free central ion concentration. The stability constants have been calculated both graphically and numerically. The graphical method has been described in an earlier paper.[5] Only some final expressions are given here.

If only mononuclear complexes exist, the following relations hold

$$X([\mathrm{L}]) = C_\mathrm{M}/[\mathrm{M}] = 1 + \sum_{j=1}^{N} \beta_j[\mathrm{L}]^j \qquad (2)$$

$$E_\mathrm{M} = RT/2F \ln X([\mathrm{L}]) \qquad (3)$$

where E_M is the difference between the emf, E, of the cell given on p. 857 and the emf, E_0, of the same cell with $C_\mathrm{L} = 0$, *i.e.* $[\mathrm{M}] = C_\mathrm{M}$.

The ligand number $\bar{n}$ for the mononuclear complexes can be calculated according to

$$\bar{n} = \sum_{j=1}^{N} j\beta_j[\mathrm{L}]^j/X \qquad (4)$$

and also by means of the approximate equation

$$\bar{n} = \frac{\Delta E_\mathrm{M}}{(RT/2F)\Delta \ln [\mathrm{L}]} \qquad (5)$$

Furthermore, n can be obtained from the slopes, k, of the straight $(C_\mathrm{L},C_\mathrm{M})$-lines of constant E_M used for the extrapolation to $C_\mathrm{M} = 0$. The numerical calculations have been performed by a least-squares program "EMK" which minimizes the following error square sum

$$U(\beta_j) = \sum_{i=1}^{N} w_i(E_{\mathrm{M},i,\mathrm{calc}} - E_{\mathrm{M},i})^2 \qquad (6)$$

where w_i is a weighting term.[15]

Calculations from the calorimetric measurements have been performed by the least-squares computer program "Kalori",[16] which minimizes the error square sum

$$U(\beta_j, \Delta H^\circ_j) = \sum_{i=1}^{N} w_i(Q_{i,\mathrm{calc}} - Q_{i,\mathrm{corr}})^2 \qquad (7)$$

By this program it is possible to treat both the enthalpy changes and the equilibrium constants as unknown parameters.

EXPERIMENTAL

Chemicals. Cadmium perchlorate was prepared by dissolving cadmium carbonate (Merck, *p.a.*) in perchloric acid (Baker Analyzed, *p.a.*). In order to avoid hydrolysis a small excess of the acid was used.[8] The cadmium concentration was determined by titration with EDTA using Erio-T as an indicator.

Cadmium amalgam, ca 9 % by weight, was prepared by dissolving sticks of cadmium metal (Baker Analyzed, *p.a.*) in mercury (*p.a.*) at 70 °C in an evacuated preparation vessel. Before use the cadmium metal was cleaned in sulfuric and perchloric acids. The amalgam was stored under nitrogen in a special storage vessel.[16]

Sodium selenocyanate was prepared from potassium selenocyanate (B.D.H.), which was first purified by three successive recrystallisations from a mixture of acetone and anhydrous ether. An approximately 5 M potassium selenocyanate solution was prepared and passed through a sodium saturated cation exchanger (Dowex 50W). The sodium selenocyanate stock solution was analyzed by potentiometric titration with silver nitrate.[17]

Zinc perchlorate, *zinc amalgam*, and *sodium perchlorate* were prepared and analyzed as described before.[5,13]

The potentiometric measurements. The emf of the following galvanic cell was measured.

$$-\ \mathrm{M(Hg)}\left|\begin{matrix} C_{\mathrm{M}}\ \mathrm{M}\ \mathrm{M(ClO_4)_2} \\ C_{\mathrm{L}}\ \mathrm{M\ NaSeCN} \\ \mathrm{NaClO_4\ to}\ I=1.00\ \mathrm{M} \end{matrix}\right|$$

$$1.00\ \mathrm{M\ NaClO_4}\left|\begin{matrix} 0.025\ \mathrm{M\ NaCl} \\ 0.975\ \mathrm{M\ NaClO_4} \end{matrix}\right|\mathrm{Ag,AgCl}\ +$$

where $\mathrm{M} = \mathrm{Zn}^{2+}$, Cd^{2+}.

A Leeds and Northrup Type K-5 Potentiometer was used, in connexion with a Leeds and Northrup Electronic D-C Null Detector, specifying a precision of ±0.01 mV. The Ag,AgCl electrodes were prepared according to Brown.[18]

The measurements were arranged as titrations. The solutions in the left-hand half-cell were obtained by adding a volume v cm^3 of a solution T to $V_0 = 15.00$ cm^3 of a solution S, where S and T had the compositions:

$$\mathrm{S:}\ \begin{cases} C_{\mathrm{M}}' & \mathrm{M\ M(ClO_4)_2} \\ (1.00 - 3C_{\mathrm{M}}') & \mathrm{M\ NaClO_4} \end{cases}$$

$$\mathrm{T:}\ \begin{cases} C_{\mathrm{L}}' & \mathrm{M\ NaSeCN} \\ (1.00 - C_{\mathrm{L}}') & \mathrm{M\ NaClO_4} \end{cases}$$

At every point during the titrations C_{M} and C_{L} were known from the compositions of the S and T solutions. As the T-solution did not contain any metal ions, C_{M} continuously decreased as C_{L} increased. The difference between the emf, E, at a certain point and the initial emf, E_0', was therefore due to dilution, as well as to the formation of complexes. To find the difference E_{M}, defined in eqn. (3), as due only to the formation of complexes, the following correction was applied.

The initial emf, E_0', is given by

$$E_0' = E_{\mathrm{k}} - (RT/2F) \ln C_{\mathrm{M}}' \tag{8}$$

where E_{k} is a constant. From E_0' and the actually measured emf E of the cell after addition of v ml, the following expression for E_{M} is easily deduced:[5]

$$E_{\mathrm{M}} = E - E_0' - (RT/2F) \ln [(V_0 + v)/V_0] \tag{9}$$

The solutions were swept by a stream of oxygen-free nitrogen to prevent oxidation of the amalgam. To obtain the correct pressure of water vapour, the nitrogen was bubbled through 1 M $\mathrm{NaClO_4}$ before entering the solutions. The potentials attained equilibrium in less than 5 min after each addition.

All titrations were repeated at least once and the reproducibility was in general within 0.15 mV for both the zinc and cadmium measurements.

As a check that the two amalgam electrodes behaved according to Nernst's law, the emf, E_0, for the cell without ligand present was measured as a function of $C_{\mathrm{M}} = [\mathrm{M}]$. These measurements were arranged as titrations where a 1.00 M $\mathrm{NaClO_4}$ solution was titrated with zinc and cadmium perchlorate solutions, respectively. For zinc the solution had a composition of $C_{\mathrm{M}} = 0.100$ M, pH = 3.6 and $I = 1.00$ M. The E_{k}-value calculated from eqn. (8) was found to be constant within ±0.05 mV for 3 mM $\leq [\mathrm{Zn}^{2+}] \leq$ 50 mM. For cadmium two different cadmium perchlorate solutions were used. The two solutions had $C_{\mathrm{M}} = 0.100$ and 0.010 M and pH = 3.5 and 5.1, respectively. Both of them had an ionic strength of 1.00 M. The E_{k}-value calculated from eqn. (8) was constant within ±0.10 mV for 0.8 mM $\leq [\mathrm{Cd}^{2+}] \leq$ 40 mM.

The calorimetric measurements. The calorimeter and the measurement technique have been described previously.[14] In each titration series, the reaction vessel initially contained V_0 cm^3 of a solution S and a titrant T was then added.

In order to determine the corrections for the heats of dilution, series analogous to those of the main measurements were performed, except that only one of the two reactants was present.

Electrical calibration showed that the heat equivalent was the same linear function of the volume added as had been found before.[19] The titration series were repeated once and the reproducibility was generally within 0.04 J.

MEASUREMENTS AND RESULTS

Potentiometric measurements on zinc selenocyanate. Four different titration series with values of C_{M}' varying from 10 to 30 mM were performed. Corresponding values of C_{L} and E_{M} from these series are collected in Table 2.

Table 2. Corresponding values of C_L and E_M for the zinc selenocyanate system.

v/ml	C_L/ mM	E_M/mV for C_M' = 10.00 mM	15.00 mM	20.00 mM	30.00 mM
0.25	13.1	0.47	0.46	0.45	0.44
0.50	25.8	0.92	0.90	0.89	0.88
0.75	38.1	1.36	1.33	1.31	1.29
1.00	50.0	1.79	1.76	1.73	1.67
1.50	72.7	2.60	2.52	2.51	2.43
2.00	94.1	3.34	3.25	3.20	3.07
2.50	114.3	4.04	3.94	3.88	3.72
3.00	133.3	4.70	4.60	4.52	4.34
3.50	151.4	5.34	5.21	5.11	4.93
4.00	168.4	5.94	5.78	5.67	5.46
5.00	200.0	7.03	6.80	6.68	6.43
6.00	228.6	8.00	7.74	7.62	7.33
7.00	254.5	8.83	8.60	8.46	8.12
8.00	278.3	9.67	9.39	9.21	8.79
9.00	300.0	10.26	10.10	9.94	9.48
10.00	320.0	10.99	10.74	10.60	10.09
12.00	355.6	12.05	11.90	11.71	11.23
14.00	386.2	13.03	12.74	12.66	12.11

Values of E_M obtained at $C_M = 2$ and 5 mM were not consistent with those of Table 2. This is certainly due to contamination of the solutions by cyanide which is formed together with red selenium, at the disintegration of selenocyanate.[4] As the cyanide complexes are much stronger than the selenocyanate ones[20] the presence of even minute amounts of cyanide ions in the selenocyanate solutions may give rise to erroneous results. The values of E_M ought moreover to be too high and increasingly so as the value of C_M decreases. This was in fact observed. In view of this it would *per se* be desirable to measure at even higher values of C_M than has in fact been done. This was not possible, however, as it would lead to an unacceptable increase in the disintegration of selenocyanate.

The pH of the solutions used had to be carefully adjusted so that decomposition of selenocyanate would not occur while the hydrolysis of the zinc ions would still be negligible. When the pH of the initial zinc solutions (S) was ≃4, no selenium was precipitated during the titrations. At the end of the titration the pH of the zinc solutions had increased from ~4 to ~7. In this range the hydrolysis of the zinc ion is slight for the concentrations used.[9]

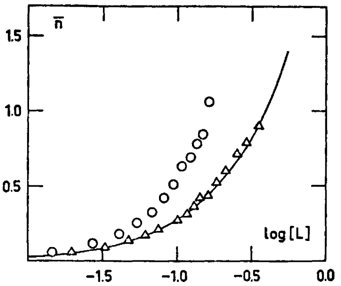

Fig. 1. The complex formation function of the zinc selenocyanate system. The fulldrawn curve has been computed from eqn. (4) while the symbols (△) refer to $\bar{n}$ found by means of eqn. (5). The values of $\bar{n}$ obtained from the slopes of the (C_M, C_L)-lines are denoted by (○) ([L] in M).

The graphical evaluation of the stability constants indicated three mononuclear complexes. In the numerical calculations, on the other hand, a good fit of the experimental data was obtained by a model including only two mononuclear complexes. The following constants were obtained.

	Graphical	Numerical
β_1/M^{-1}	2.90 ± 0.08	2.74 ± 0.09
β_2/M^{-2}	3.90 ± 0.8	4.4 ± 0.4
β_3/M^{-3}	4.5 ± 2.0	

The errors given for the graphically calculated constants are subjectively estimated. For the numerical determination they correspond to three standard deviations. In the range of [L] studied the concentration of a hypothetical complex ML_3 will not exceed 5 % of C_M. It is thus not possible to decide with certainty from these measurements whether a third complex is formed or not.

The numerically found set of constants is considered to be the 'best' one and is used in the following. The complex formation function, $\bar{n}$([L]), computed according to eqn. (4), is given in Fig. 1 as a fulldrawn curve. The values of $\bar{n}$ obtained from the slopes of the (C_M, C_L)-lines deviate. This can be explained, however, by the contamination by cyanide ions, which will give too high E_M-values, especially for the series with the lowest value of C_M (= 10 mM). This could also be seen in the numerical calculations where the deviations $(E_M - E_{M,calc})$ have mainly positive signs in this series. The

Table 3. Determination of heats of dilution for sodium selenocyanate. $V_0 = 90.00$ cm³ and $V = (V_0 + v)$ cm³.

S: $C_{\mathrm{NaClO_4}} = 1.000$ M. T: $C_{\mathrm{NaSeCN}} = 1.000$ M.

v/cm³, $-Q_{\mathrm{dil}}$/J: *3.000*, 0.594; *6.000*, 0.551; *9.000*, 0.516; *12.00*, 0.484; *15.00*, 0.462; *18.00*, 0.440; *21.00*, 0.424; *24.00*, 0.406; *27.00*, 0.390.

relatively low value of the standard deviation, 0.14 mV, indicates that the influence of the cyanide ions in the measurements has been satisfactorily suppressed.

Calorimetric measurements on zinc selenocyanate. Three different titration series with $C_{\mathrm{M}} = 20$, 30, and 50 mM have been carried out, Tables 3 and 4. In all series ligand was added to a solution of the metal ion. In this way a total selenocyanate concentration of $\simeq 200$ mM could be reached before selenium was precipitated. In an attempt to reach higher values of [L] a metal solution was added to a ligand solution. This titration, however, was unsuccessful. When the pH was low enough to prevent hydrolysis of the zinc ion, the selenocyanate ion disintegrated rapidly. From the stability constants obtained before it was evident that the concentration of a third complex, if formed, was negligible in the range of concentration used. Due to weak complex formation and low values of ΔH°_j, the measured heat effects were small. It was therefore impossible to determine the stability constants from the calorimetric data. In the calculation of the enthalpy changes by the program "Kalori", sets of stability constants including two as well as three complexes were tried. A good fit, $\sigma Q_{\mathrm{corr}} = 0.032$ J, was achieved with the two stability constants obtained in the numerical calculation of the potentiometric measurements. Introduction of a third complex did not give any significantly better fit ($\sigma Q_{\mathrm{corr}} = 0.028$ J). The numerically obtained values of β_1 and β_2 together with computed values of ΔG°_j, ΔH°_j and ΔS°_j are given in Table 8. In Fig. 2, Δh_v is plotted *versus* $\bar{n}$. Evidently no variation of Δh_v with C_{M} can be discerned, which indicates that no polynuclear complexes are formed. The fulldrawn curve is calculated from the stability constants and enthalpy changes given in Table 8.

Table 4. Determination of the heats of formation for the zinc selenocyanate complexes. For all the series: $V_0 = 90.00$ cm³ and $V = (V_0 + v)$ cm³.

(a) ○ S: $C_{\mathrm{M}} = 0.05000$ M, $C_{\mathrm{NaClO_4}} = 0.850$ M.
T: $C_{\mathrm{L}} = 0.800$ M, $C_{\mathrm{NaClO_4}} = 0.200$ M.

v/cm³, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 1.697, −0.067; *6.000*, 1.437; 0.025; *9.000*, 1.283, 0.030; *12.00*, 1.188, −0.006; *15.00*, 1.071, −0.006; *18.00*, 0.996, −0.033; *21.00*, 0.894, −0.021; *24.00*, 0.810, −0.017; *27.00*, 0.746, −0.024;

(b) □ S: $C_{\mathrm{M}} = 0.03000$ M, $C_{\mathrm{NaClO_4}} = 0.910$ M.
T: $C_{\mathrm{L}} = 0.800$ M, $C_{\mathrm{NaClO_4}} = 0.200$ M.

v/cm³, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 1.038, −0.013; *6.000*, 0.883, 0.032; *9.000*, 0.791, 0.026; *12.00*, 0.705, 0.026; *15.00*, 0.633, 0.022; *18.00*, 0.568, 0.021; *21.00*, 0.523, 0.008; *24.00*, 0.466, 0.015; *27.00*, 0.448, −0.012;

(c) △ S: $C_{\mathrm{M}} = 0.02000$ M, $C_{\mathrm{NaClO_4}} = 0.940$ M.
T: $C_{\mathrm{L}} = 0.800$ M, $C_{\mathrm{NaClO_4}} = 0.200$ M.

v/cm³, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 0.743, −0.043; *6.000*, 0.581, 0.042; *9.000*, 0.506, 0.049; *12.00*, 0.450, 0.045; *15.00*, 0.396, 0.046; *18.00*, 0.384, 0.013; *21.00*, 0.370, −0.013; *24.00*, 0.362, −0.040; *27.00*, 0.349, −0.058;

Potentiometric measurements on cadmium selenocyanate. The experimental results are collected in Tables 5a and 5b. Two different ligand solutions with $C_{\mathrm{L}} = 0.200$ and 1.000 M, respectively, were added to four different cadmium solutions, with values of C_{M}' varying from 5 to 40 mM. The values of the pH of these solutions were 5 − 5.5. It is possible to use higher values of pH in cadmium than in zinc solutions.

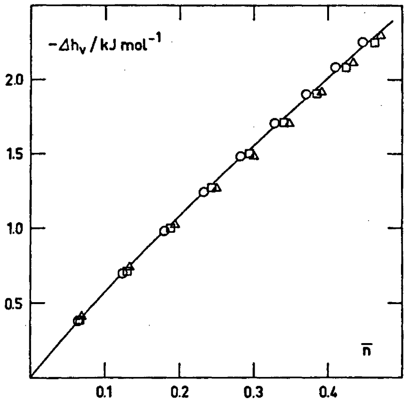

Fig. 2. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the zinc selenocyanate system, *cf*. Table 4.

Table 5a. Corresponding values of C_L and E_M for the cadmium selenocyanate system.

v/ml	C_L/ mM	E_M/mV for C_M' = 5.00 mM	10.00 mM	20.00 mM	40.00 mM
0.25	3.28	1.07	0.97	0.80	0.60
0.50	6.45	2.06	1.87	1.56	1.18
0.75	9.52	2.99	2.73	2.29	1.75
1.00	12.50	3.89	3.55	3.01	2.33
1.25	15.38	4.73	4.34	3.71	2.89
1.50	18.18	5.55	5.10	4.39	3.45
1.75	20.9	6.31	5.81	5.04	3.98
2.00	23.5	7.03	6.51	5.67	4.50
2.50	28.6	8.42	7.82	6.88	5.54
3.00	33.3	9.67	9.02	8.00	6.52
3.50	37.8	10.83	10.16	9.07	7.47
4.00	42.1	11.90	11.19	10.05	8.35
4.50	46.2	12.91	12.18	10.99	9.21
5.00	50.0	13.85	13.10	11.89	10.01
5.50	53.7	14.75	13.98	12.73	10.79
6.00	57.1	15.60	14.81	13.53	11.54
6.50	60.5	16.39	15.59	14.30	12.26
7.00	63.6	17.17	16.32	15.01	12.94
8.00	69.6	18.57	17.71	16.35	14.22
9.00	75.0	19.83	18.96	17.58	15.40
10.00	80.0	20.99	20.10	18.71	16.50
11.00	84.6	22.05	21.15	19.74	17.51
12.00	88.9	23.07	22.13	20.71	18.46
13.00	92.9	23.97	23.02	21.61	19.35
14.00	96.6	24.81	23.86	22.44	20.18
15.00	100.0	25.60	24.55	23.24	20.97

Table 5b. Corresponding values of C_L and E_M for the cadmium selenocyanate system.

v/ml	C_L/mM	E_M/mV for C_M' = 5.00 mM	10.00 mM	20.00 mM
0.25	16.4	4.98	4.58	3.84
0.50	32.3	9.18	8.53	7.43
0.75	47.6	12.99	12.15	10.72
1.00	62.5	16.45	15.46	13.82
1.25	76.9	19.73	18.62	16.74
1.50	90.9	22.73	21.54	19.47
1.75	104.5	25.62	24.31	22.06
2.00	117.6	28.39	26.98	24.54
2.25	130.4	31.04	29.57	26.96
2.50	142.9	33.61	32.00	29.28
2.75	154.9	36.03	34.36	31.50
3.00	166.7	38.30	36.64	33.65
3.25	178.1	40.52	38.82	35.76
3.50	189.2	42.68	40.88	37.77
3.75	200.0	44.67	42.88	39.70
4.00	210.5	46.58	44.79	41.59
4.25	220.8	48.47	46.66	43.42
4.50	230.8	50.21	48.41	45.15
5.00	250.0	53.49	51.71	48.47
5.50	268.3	56.51	54.77	51.58
6.00	285.7	59.27	57.57	54.46
6.50	302.3	61.82	60.18	57.14
7.00	318.2	64.17	62.57	59.61
7.50	333.3	66.31	64.79	61.94
8.00	347.8	68.31	66.89	64.10
8.50	361.7	70.24	68.81	66.12
9.00	375.0	71.99	70.62	68.01
9.50	387.8	73.62	72.30	69.79
10.00	400.0	75.14	73.86	71.45
11.00	423.1	77.88	76.73	74.48
12.00	444.4	80.37	79.29	77.18
13.00	464.3	82.63	81.57	79.58
14.00	482.8	84.63	83.63	81.75
15.00	500.0	86.36	85.46	83.72

First, a higher initial value could be applied as the cadmium ion is a weaker acid than the zinc ion. Second, stronger selenocyanate complexes are formed by cadmium than by zinc. As the complexes are certainly less acidic than the hydrated ions this means that the hydrolysis is more completely suppressed in the cadmium solutions. The relatively high values of pH that could be used in the cadmium selenocyanate solutions also ensured that these became completely stable. This is indicated by the fact that the results from the titration series with lowest cadmium ion concentration (C_M' = 5 mM) are quite in line with the results from the other series.

Both the graphical and numerical calculation of the stability constants indicated four mononuclear complexes, Table 7. In the graphical determination of the β_j-values the X_3-function was linear up to [L] = 300 mM, but showing a positive deviation at higher values of [L]. This may of course be interpreted as a fifth complex. It is more likely, however, that the deviation is due to changes in the activity coefficients brought about by complex formation and by the progressive exchange of ClO_4^- for $SeCN^-$. Furthermore, at high ligand concentration there may be some disintegration of $SeCN^-$, giving cyanide ions (*cf.* p. 858). At [L] = 300 mM more than 60 % of the total amount of cadmium is in the form of the fourth complex. This means that a good value of β_4 should be obtained from the measurements up to [L] = 300 mM. Data from higher values of [L] were not considered in the graphical evaluation of the β_j-values. Results from two different numerical calculations are also given in Table 7. In the first of these all measured data are included and in the

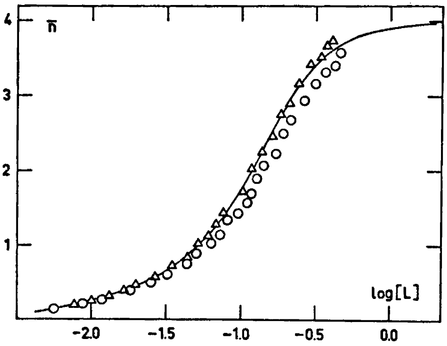

Fig. 3. The complex formation function of the cadmium selenocyanate system. The fulldrawn curve has been computed from eqn. (4) while the symbols (△) refer to $\bar{n}$ found by means of eqn. (5). The values of $\bar{n}$ obtained from the slopes of the (C_M,C_L)-lines are denoted by (○) ([L] in M).

second only those for $C_L < 380$ mM. As expected the results from the latter calculation agree quite well with the results found graphically, while the former calculation naturally yields a higher value of β_4, and a correspondingly lower value of β_3.

The complex formation curve, $\bar{n}$[L]), computed from the graphically obtained set of constants according to eqn. (4) is given in Fig. 3 as a fulldrawn curve. The values of $\bar{n}$ obtained from eqn. (5) agree very well with this curve and also those obtained from the slopes of the (C_M, C_L)-lines fit quite satisfactorily. Only a minor systematic deviation is observed.

Calorimetric measurements on cadmium selenocyanate. In three of the seven titration series carried out ligand was added to a solution of the metal ion (Table 6, a–e). In four series (d–g), metal ions were added to a solution of the ligand, in order to bring about a larger formation of the higher complexes. The metal ion solutions had a pH ≃ 5.5. When ligand was added to cadmium solution the corrected heats, Q_{corr}, were obtained by subtracting the heats of dilution for the ligand (given in Table 3) from the experimentally measured heat effects, as the heats of dilution of the metal ions were negligible in these cases. When cadmium solution was added to the ligand solution, heats of dilution for both metal and ligand had to be introduced.

As the complexes formed are moderately

Table 6. Determination of the heats of formation for the cadmium selenocyanate complexes. For all series: $V_0 = 90.00$ cm^3 and $V = (V_0 + v)$ cm^3.

(a) ▽ S: $C_M = 0.02000$ M, $C_{NaClO_4} = 0.940$ M.
T: $C_L = 1.000$ M.

v/cm^3, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 9.625, −0.037; *6.000*, 7.053, 0.030; *9.000*, 5.817, −0.042; *12.00*, 5.094, −0.030; *15.00*, 4.496; 0.029; *18.00*, 3.945, 0.071; *21.00*, 3.480, 0.036; *24.00*, 3.014, 0.025; *27.00*, 2.573, 0.032;

(b) □ S: $C_M = 0.01500$ M, $C_{NaClO_4} = 0.955$ M.
T: $C_L = 1.000$ M.

v/cm^3, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 7.677, 0.014; *6.000*, 5.436, 0.071; *9.000*, 4.541, −0.056; *12.00*, 3.960, −0.033; *15.00*, 3.494, −0.020; *18.00*, 3.032, 0.003; *21.00*, 2.579, 0.032; *24.00*, 2.209, 0.012; *27.00*, 1.900, −0.022;

(c) ○ S: $C_M = 0.01000$ M, $C_{NaClO_4} = 0.970$ M.
T: $C_L = 1.000$ M.

v/cm^3, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 5.479, 0.022; *6.000*, 3.757, 0.052; *9.000*, 3.143, −0.038; *12.00*, 2.742, −0.036; *15.00*, 2.355, 0.005; *18.00*, 2.047, −0.025; *21.00*, 1.713, −0.007; *24.00*, 1.422, 0.005; *27.00*, 1.303, −0.112;

(d) ▲ S: $C_L = 0.500$ M, $C_{NaClO_4} = 0.500$ M.
T: $C_M = 0.1000$ M, $C_{NaClO_4} = 0.700$ M.

v/cm^3, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 9.987, 10.314, −0.021; *6.000*, 9.812, 10.103, −0.026; *9.000*, 9.624, 9.888, −0.045; *12.00*, 9.347, 9.607; −0.014; *15.00*, 9.126, 9.367, −0.040;

(e) ● S: $C_L = 0.400$ M, $C_{NaClO_4} = 0.600$ M.
T: $C_M = 0.1000$ M, $C_{NaClO_4} = 0.700$ M.

v/cm^3, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 9.547, 9.810, 0.004; *6.000*, 9.297, 9.521, −0.012; *9.000*, 8.980, 9.175, 0.007; *12.00*, 8.540, 8.729, 0.104; *15.00*, 8.363, 8.530, −0.064;

(f) ▼ S: $C_L = 0.300$ M, $C_{NaClO_4} = 0.700$ M.
T: $C_M = 0.1000$ M, $C_{NaClO_4} = 0.700$ M.

v/cm^3, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 8.792, 8.964, 0.031; *6.000*, 8.349, 8.502, 0.043; *9.000*, 7.903, 8.043, 0.030; *12.000*, 7.494, 7.610, −0.021; *15.00*, 6.992, 7.091, 0.013;

(g) ■ S: $C_L = 0.200$ M, $C_{NaClO_4} = 0.800$ M.
T: $C_M = 0.1000$ M, $C_{NaClO_4} = 0.700$ M.

v/cm^3, Q_{exp}/J, Q_{corr}/J, ΔQ_{corr}/J: *3.000*, 7.284, 7.413, 0.046; *6.000*, 6.687, 6.809, 0.019; *9.000*, 6.127, 6.237, −0.014; *12.00*, 5.548, 5.657, 0.010; *15.00*, 5.149, 5.241, −0.078;

Table 7. Stability constants for the cadmium selenocyanate system obtained from potentiometric and calorimetric measurements. The errors correspond to three standard deviations given by the computer or to estimated errors. Parameters printed in italics were not varied.

Method	β_1/M^{-1}	β_2/M^{-2}	β_3/M^{-3}	β_4/M^{-4}	U	
Pot., graphically	29.0 ± 0.5	200 ± 30	700 ± 200	11 000 ± 1 000		
Pot., by computer	29.6 ± 0.9	235 ± 30	350 ± 250	12 300 ± 600		all points incl.
Pot., by computer	30.1 ± 0.9	210 ± 30	650 ± 300	11 300 ± 900		$C_L \leq$ 375 mM
Cal.	*29.5*	228	800	*11 000*	0.0746	
Cal.	*29.5*	*228*	760	10 400	0.0740	
Cal.	*29.5*	140	680	8 800	0.0634	
Proposed values	29.5 ± 0.5	200 ± 30	700 ± 200	11 000 ± 1 000	0.0778	

strong, and the heat effects fairly large, a determination of the stability constants from the calorimetric data should be possible. Nevertheless, a complete determination of the stability constants in this manner turned out to be impossible, because of the narrow range of existence of especially the third complex. We have therefore to introduce one or two of the constants calculated from the potentiometric measurements as known parameters in the "Kalori" calculation thereby reducing the number of unknown parameters. In the first hand the value of β_1 ($= 29.5$ M^{-1}) seems to be well established and was therefore not varied in the computations. The constants $\beta_2 - \beta_4$ were on the other hand treated as either known or unknown parameters in different combinations. The results from some of these calculations are given in Table 7. As can be seen the calorimetrically obtained values of $\beta_2 - \beta_4$ are quite in line with those obtained potentiometrically. A 'best' set of values has been proposed, Table 7. These β_j-values and corresponding values of ΔG°_j, ΔH°_j and ΔS°_j are listed in Table 8. In Fig. 4 the Δh_v-function is plotted *versus* $\bar{n}$, calculated from the 'best' β_j-values. The function is independent of C_M, which once more proves that no polynuclear complexes

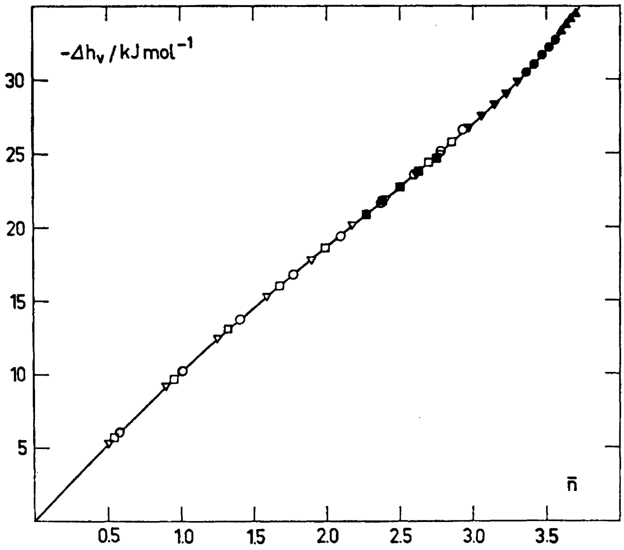

Fig. 4. The total molar enthalpy change, Δh_v, as a function of $\bar{n}$, for the cadmium selenocyanate system, *cf.* Table 6.

Table 8. The stability constants used and the computed values of $\Delta G°_j$, $\Delta H°_j$ and $\Delta S°_j$ for the stepwise reactions of the zinc and cadmium selenocyanate and thiocyanate systems. The data for the thiocyanate systems are taken from Ref. 5. The errors given correspond to three standard deviations or to estimated errors.

System		$Zn^{2+} - SeCN^-$	$Zn^{2+} - SCN^-$	$Cd^{2+} - SeCN^-$	$Cd^{2+} - SCN^-$
β_j/M^{-j}	$j = 1$	2.74 ± 0.09	5.10 ± 0.03	29.5 ± 0.5	20.7 ± 0.5
	2	4.4 ± 0.4	11.0 ± 0.6	200 ± 30	97 ± 5
	3		15.0 ± 3.6	700 ± 200	107 ± 20
	4		32 ± 5	$11\,000 \pm 1\,000$	75 ± 30
$\frac{-\Delta G°_j}{\text{kJ mol}^{-1}}$	1	2.50 ± 0.08	4.04 ± 0.02	8.39 ± 0.04	7.53 ± 0.08
	2	1.17 ± 0.25	1.91 ± 0.14	4.7 ± 0.4	3.85 ± 0.08
	3		0.76 ± 0.6	3.1 ± 0.9	0.3 ± 0.7
	4		1.9 ± 0.8	6.8 ± 0.9	-0.9 ± 1.6
$\frac{-\Delta H°_j}{\text{kJ mol}^{-1}}$	1	5.95 ± 0.17	5.80 ± 0.15	10.05 ± 0.10	9.58 ± 0.04
	2	0.4 ± 0.6	1.8 ± 1.0	16.3 ± 1.0	8.08 ± 0.38
	3		0.8 ± 3.0	13.5 ± 1.0 [a]	9.2 ± 3.8
	4		7.7 ± 3.5		
$\frac{\Delta S°_j}{\text{J mol}^{-1}\text{ K}^{-1}}$	1	-11.6 ± 0.7	-5.9 ± 0.5	-5.6 ± 0.3	-6.7 ± 0.4
	2	3 ± 3	0 ± 4	-39 ± 4	-14 ± 1.3
	3		0 ± 10	-12 ± 4 [a]	-30 ± 13
	4		-19 ± 12		

[a] For the individual steps of the third and fourth steps we obtain $\Delta H°_3 = 23 \pm 7$, $\Delta H°_4 = -37 \pm 7$, $\Delta S°_3 = 90 \pm 20$, $\Delta S°_4 = -100 \pm 30$.

exist. The fulldrawn curve is calculated from the stability constants and enthalpy changes given in Table 8.

DISCUSSION

In agreement with Humffray *et al.*[10] we find two complexes in the zinc selenocyanate and four in the cadmium selenocyanate system. For the zinc selenocyanate our values of β_j are lower, however, than those given by Humffray *et al.*[10] while for the cadmium selenocyanate the situation is reversed. With the exception of β_4 of the cadmium selenocyanate system, the differences of the β_j-values of the two investigations are not very large, however, and they may be explained by differences in medium and temperature of the two investigations. For the cadmium selenocyanate system our values of $\beta_1 - \beta_3$ are in line with those reported by Golub and Andreichenko.[12] while the value of β_4 given by these authors is considerably lower than ours. Golub and Andreichenko [12] also postulate a fifth complex but this seems hazardous in view of the rather scarce experimental material.

Thiocyanate and selenocyanate are ambidentate ligands coordinating *via* N or S and *via* N or Se, respectively. Soft metals prefer the S and Se atoms, while hard metals prefer the harder N-atom. Selenium donors are generally found to be softer than analogous sulfur donors [21] and should therefore give stronger complexes with soft acceptors. Therefore, if an acceptor is coordinated *via* the S and Se atoms, the selenocyanate complexes should be stronger than the thiocyanate ones. If, on the other hand, the N-atoms are coordinated, the strengths of the thiocyanate and selenocyanate complexes should be much the same.

The selenocyanate complexes of cadmium are somewhat stronger than the thiocyanate complexes, while the reverse holds for the corresponding zinc complexes, Table 8, though the differences are not very large. The results clearly support the deductions drawn from infrared spectroscopy [22] that the thiocyanate and selenocyanate ions are bonded to the borderline acceptor Cd^{2+}, at least partly, *via* the S and Se atoms, respectively, while coordination to the hard Zn^{2+} occurs *via* the N-atoms.

In the discussion of the enthalpy and entropy changes accompanying the complex formation, the strength of the bond formed between metal and ligand as well as hydration effects have to be considered. The two donor atoms in the thiocyanate and selenocyanate ions are both negatively charged and should consequently be more or less hydrated. From MO-calculations Wagner[23] has found that the nitrogen atoms in the two ligands have the same atomic charge of ≈ -0.4 while the sulfur and selenium atoms have charges of -0.71 and -0.84, respectively. The ratio atomic charge/radius for the sulfur and selenium atoms is about the same (0.58). Thus, it is reasonable to assume that in the free ligands the S and Se atoms are about equally hydrated, as are the two nitrogen atoms.

For both thiocyanate and selenocyanate the charge density on the non-bonding end decreases upon coordination. Wagner[23] has shown by calculations on the corresponding acids that upon coordination *via* the N-atoms the decrease of charge is larger on the sulfur atom than on the selenium atom. Thus if an acceptor is coordinating *via* the N-atoms, more water should be liberated from the S atom in thiocyanate than from the Se atom in selenocyanate. Consequently, the entropy term should be more positive or less negative for the thiocyanate reaction than for the selenocyanate reaction. If coordination, on the other hand, occurs through the S or Se atoms, the same amount of water should be set free from the non-bonding N atom for both ligands. Thus the entropy terms for the two reactions should be about the same.

As seen from Table 8, $\Delta S°_1$ for the formation of zinc thiocyanate is less negative than $\Delta S°_1$ for the formation of zinc selenocyanate. In the reactions with Cd^{2+}, on the other hand, the two ligands give about the same value of $\Delta S°_1$. This evidently fits with the postulated N-bonding of Zn^{2+}, and the preferred S and Se bonding of Cd^{2+}.

The preference for selenium donors over analogous sulfur donors generally exhibited by soft acceptors (p. 863) is mainly due to more negative values of $\Delta H°_j$.[21] This indicates that the Se donors are preferred because of their stronger covalent bonding capacity. Thus if an acceptor coordinates thiocyanate and selenocyanate ions *via* their S and Se donor atoms, respectively, the selenocyanate complexes should be formed in more exothermic reactions than the thiocyanate complexes. If, on the other hand, an acceptor prefers to coordinate these ligands *via* their harder N-atoms, the reactions will be less exothermic than in the case of S or Se coordination. Moreover, the strength of the bonds will be little influenced by an exchange of S for Se and about the same values of $\Delta H°_j$ may therefore be expected for thiocyanate and selenocyanate complexes.

The enthalpy changes are much the same for zinc thiocyanate and selenocyanate, Table 8. The complexes are formed in weakly exothermic reactions. For cadmium the enthalpy changes are more exothermic for selenocyanate than for thiocyanate. The complexes are formed in more exothermic reactions than the corresponding zinc complexes. This once more indicates that thiocyanate and selenocyanate are coordinated to Cd^{2+}, at least partly, *via* the S and Se atoms, respectively, and to Zn^{2+} *via* the N-atoms.

For complexes formed between hard or borderline acceptors and donors a fairly regular decrease of $\Delta S°_j$ generally occurs for each consecutive step.[24] For the zinc selenocyanate and thiocyanate systems this is obviously not the case, Table 8. In both systems $\Delta S°_2$ is higher than $\Delta S°_1$. This deviation is probably caused by a change of coordination at the second step.[24] The switch most probably takes place between the octahedral coordination represented by the initial hexaquo ion $Zn(H_2O)_6^{2+}$ and the tetrahedral coordination represented by the final complex ZnL_4^{2-}. Such a change of coordination should be followed by a liberation of a large amount of water from the hydration shell, resulting in especially high values of both $\Delta H°_2$ and $\Delta S°_2$. For the halide and acetate systems of Zn^{2+} an even more pronounced increase of $\Delta H°_2$ and $\Delta S°_2$ is observed,[25] strongly suggesting a change of coordination configuration at this very step also for these systems.

For the cadmium selenocyanate system the values of $\Delta H°_3$ and $\Delta S°_3$ are abnormally high. Also the hexaaquo ion $Cd(H_2O)_6^{2+}$ has most likely an octahedral coordination while the final complex, $Cd(SeCN)_4^{2-}$, is tetrahedral. The high values of $\Delta H°_3$ and $\Delta S°_3$ are most probably due to the fact that at least the main part of this change of coordination takes place at the third step. For the halide systems of Cd^{2+} a similar but less marked reversal of the enthalpy and entropy changes at the third step is observed.[25] Also for these systems the same switch of coordination seems to occur at the same stage.

Remarkably enough no reversal is observed for the cadmium thiocyanate system. The switch from octahedral to tetrahedral coordination which most likely takes place also in this system cannot therefore occur more or less exclusively at the third or any other particular step. Rather it must be spread out over several steps as has been postulated before for other systems where no drastic reversals between consecutive values of ΔS°_j and ΔH°_j are observed, in spite of the fact that a change of coordination no doubt takes place between the initial and final complexes.[24]

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