Studies on Ion Association: Thermodynamics of Formation of Monoselenocyanato-complexes of Cobalt(II), Nickel(II), and Cadmium(II)

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Free-energy and enthalpy changes of formation of monoselenocyanato-complexes of Co^{II}, Ni^{II}, and Cd^{II} have been determined by potentiometry and calorimetry respectively. The stabilities of the selenocyanato-complexes are slightly lower than the corresponding thiocyanato-complexes. The thermodynamic data suggest that whereas $[SCN]^-$ ion co-ordinates with Cd^{2+} through either the N or S atom, $[SeCN]^-$ does so exclusively through the N atom.

THE thermodynamics of complex formation of monothiocyanato-complexes of bivalent metal ions have been studied by both potentiometry[1] and calorimetry.[2] Selenocyanate ion has similar complex-forming properties as thiocyanate. It was, therefore, useful to study the thermochemistry of formation of selenocyanato-complexes for comparison. Although Toropova[3] made a preliminary study of the nature of cadmium(II) selenocyanate in an aqueous medium by polarography and potentiometry, precise data are not available in the literature for stabilities and other thermodynamic functions (ΔH and ΔS of formation) of selenocyanato-complexes in aqueous media.

EXPERIMENTAL

Chemicals and Reagents.—All chemicals were of analytical grade. Solutions were prepared in triply distilled water. Solutions of metal perchlorates were prepared from the respective carbonates by adding excess of carbonate in perchloric acid, digesting in a water-bath, and subsequently estimating by standard gravimetric methods.

$$\begin{array}{c|c||c||c|c} \mathrm{Ag,\ Ag[SeCN](s)} & \mathrm{K[SeCN](aq)}(c_1) & \text{Saturated} & \mathrm{K[SeCN](aq)}(c_1) & \mathrm{Ag[SeCN](s)Ag} \\ & & \mathrm{[NH_4][NO_3]}\ \text{bridge} & & \\ & \mathrm{M[ClO_4]_2(aq)}(c_2) & & & \end{array}$$

Half-cell (I) Half-cell (II)

Determination of Stability Constants.—Thermodynamic stability constants and hence standard free-energy changes of complex formation were determined by potentiometry using a silver–silver(I) selenocyanate electrode developed in this laboratory.[4] A concentration cell of type shown below was used. In a study of thiocyanato-complexes in a cell of this type it was observed that the liquid-junction potential is negligibly small.[1,5] The electrode set-up was kept inside an air thermostat maintained at 25 ± 0.1 °C.

The e.m.f. of the cell is given by expression (1) where

$$E = \frac{2.303\,RT}{nF} \log \frac{a_{\mathrm{SeCN^-}}^{(\mathrm{II})}}{a_{\mathrm{SeCN^-}}^{(\mathrm{I})}} \qquad (1)$$

$a_{\mathrm{SeCN^-}}^{(\mathrm{II})}$ and $a_{\mathrm{SeCN^-}}^{(\mathrm{I})}$ are the activities of the $SeCN^-$ ion in the half-cells (II) and (I) respectively. Knowing $a_{\mathrm{SeCN^-}}^{(\mathrm{II})}$ from the concentration c_1, $a_{\mathrm{SeCN^-}}^{(\mathrm{I})}$ could be calculated. The concentration of free selenocyanate in the mixture [half-cell (I)], which gives the concentrations of the other species, may be determined if the activity coefficient, $f_{\mathrm{SeCH^-}}$, is known from the ionic strength. To obtain the ionic strength and concentration of the various species in the mixture a series of approximations and refinements were made as previously[5] until constant values were obtained. From

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[1] R. C. Das, A. C. Dash, D. Satyananayana, and U. N. Dash, *Thermochim. Acta*, 1971, **2**, 435.

[2] G. H. Nancollas and K. Torrance, *Inorg. Chem.*, 1967, **6**, 1567.

[3] V. F. Toropova, *Zhur. neorg. Khim.*, 1956, **1**, 243.

[4] R. C. Das, G. Sahu, D. Satyanarayana, and S. N. Misra, *Electrochim. Acta*, 1974, **19**, 887.

[5] R. C. Das, A. C. Dash, and J. P. Misra, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2417.

these calculations it was found that, under our conditions, $[M(SeCN)_2]$ species ($M = Co^{II}$, Ni^{II}, and Cd^{II}) exist in negligible concentration. Hence only the first association

$$\underset{(c_2 - x)}{M^{2+}} + \underset{(c_1 - x)}{SeCN^-} \rightleftharpoons \underset{x}{[M(SeCN)]^+} \qquad (2)$$

(2) was considered. The thermodynamic equilibrium constant is given by equation (3) (assuming $f_{SeCN^-} = f_{M(SeCN)^+}$).

$$K = \frac{a_{M(SeCN)^+}}{a_{M^{2+}}\, a_{SeCN^-}} = \frac{x}{(c_2 - x)(c - x)} \cdot \frac{1}{f_{M^{2+}}} \qquad (3)$$

The calculation assumes that potassium selenocyanate and the metal perchlorates are completely dissociated. Although perchlorate ion is known to form complexes in solution with some metal ions including Cd^{II}, the interaction is so small that no complex formation was detected except at very high $[ClO_4^-]$ (3M or above).[6,]* The Davies[7] equation, (4), was used to calculate activity coefficients of the ions from the ionic strength of the solutions.

$$-\log f_i = Az_i^2 \left(\frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0.2\, I \right) \qquad (4)$$

Determination of Enthalpies.—The enthalpy change of association was obtained by direct calorimetry. The calorimeter consisted of a Dewar flask, further insulated by Polythene, painted aluminium, and an asbestos jacket, through which the electrical leads and stirrer passed. The entire unit was placed in a thermostat controlled within ±0.05 °C. The reaction was carried out inside the Dewar flask and the temperature change was measured by means of a resistance thermometer, consisting of sensitive thermistors. The resistance of the thermistors was measured up to 0.1 Ω by means of a conventional Wheatstone bridge in conjunction with a spot galvanometer. The magnitude of dT/dR was *ca.* 1×10^{-6} °C S.

To determine ΔH, $(250 - V)$ cm^3 of metal(II) perchlorate were placed in the reaction vessel and V cm^3 (varied between 3 and 6 cm^3) of potassium selenocyanate solution of appropriate concentration was added instantaneously. The heat change was measured within a few seconds of mixing and then at intervals of 15 s for *ca.* 1.5 min. The readings were plotted against time and the extrapolated value to zero time was taken for the following calculation.

The heat liberated in the calorimeter on mixing potassium selenocyanate and metal(II) perchlorate is related to the enthalpy, ΔH, of reaction (2) by equation (5), where q and V

$$-q = x \Delta H V \qquad (5)$$

represent the heat liberated and the volume of the solution (0.25 l) respectively; x can be obtained from the equilibrium constant with the help of equation (3) if $f_{M^{2+}}$ is known. For the simultaneous determination of x and $f_{M^{2+}}$, a series of approximations and refinements, as in the potentiometric determination of K, was made until constant values of x and I were obtained. In this calculation, the heat change due to the dilution of the potassium selenocyanate solution (from V to 250 cm^3) was ignored as it was observed in separate experiments that this heat change was much less than that due to ion association between M^{2+} and $[SeCN]^-$ and was within the experimental uncertainty.

TABLE 1

Stability constants of $[M(SeCN)]^+$ complexes at 25 °C

	Composition of half-cell (II)	Composition of half-cell(I)			
Metal ion	$10^2[K(SeCN)]/M$	$10^2[K(SeCN)]_T/M$	$10^2[M(ClO_4)_2]_T/M$	Mean e.m.f./V	K/l mol^{-1}
Cd^{2+}	1.875	1.875	5.00	0.02975	112.7
	1.736	1.736	4.00	0.02405	89.1
	1.735	1.736	5.00	0.02730	91.8
	1.736	1.736	6.00	0.02290	87.5
	2.083	2.083	5.00	0.02960	93.1
	2.083	2.083	6.00	0.03070	101.6
				Mean	96.0 ± 9.6
Ni^{2+}	3.000	3.000	8.00	0.0184	44.7
	2.323	2.323	6.00	0.0200	59.2
	2.083	2.083	3.88	0.0146	49.7
	2.232	2.232	8.00	0.0178	35.9
	1.736	1.736	2.92	0.0139	37.0
				Mean	45.3 ± 9.6
Co^{2+}	1.806	1.806	7.41	0.0199	30.8
	1.806	1.806	8.15	0.0215	33.5
	1.445	1.445	7.41	0.0217	36.6
	1.245	1.245	3.24	0.0128	25.6
	1.245	1.245	3.55	0.0140	28.8
	1.245	1.245	4.26	0.0154	30.3
				Mean	30.9 ± 3.8

RESULTS AND DISCUSSION

Table 1 gives the stability constants of $[M(SeCN)]^+$ complexes ($M = Co^{II}$, Ni^{II}, and Cd^{II}) at 25 °C; Mn^{II} and Zn^{II} systems were tried but did not give reproducible results. It is worthwhile to compare the stability constants of selenocyanato-complexes at 25 °C with those of thiocyanato-complexes obtained by similar methods. Table 2 shows that the selenocyanato-complexes are slightly weaker. Purely from electrostatic considerations, selenocyanato-complexes are expected to be less

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* $1M = 1$ mol dm^{-3}.

[6] M. T. Beck, 'Chemistry of Complex Equilibria,' van Nostrand, 1970, p. 28.

[7] C. W. Davies, *J. Chem. Soc.*, 1938, 2093; 'Ion Association,' Butterworths, 1962.

stable due to the comparatively large size of the $[SeCN]^-$ ion; although the complexes are predominantly covalently bonded, there will be some 'ionic character' in the bonds.

TABLE 2

Comparison of stabilities of thiocyanato- and selenocyanato-complexes at 25 °C

Metal ion	Mn^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Cd^{2+}
$\log K$ for $[M(SCN)]^+$	1.15	1.87	1.98	1.49	2.15
$\log K$ for $[M(SeCN)]^+$		1.49	1.66		1.98

Thermodynamic Functions.—Table 3 gives the calorimetric results. The ΔH values reported are for the experimental range of ionic strength (generally between 0.08 and 0.15M). The value corresponding to zero ionic strength (ΔH^0) is related to ΔH through equation (6)

$$\Delta H - 2.303\,RT^2[\partial \log f_{M^{2+}}/\partial T] = \Delta H^0 \qquad (6)$$

which can be easily derived from (3). The term $(\partial \log f_{M^{2+}}/\partial T)$ is unknown and likely to be small. Moreover, preliminary observations showed the ΔH values to be insensitive to ionic strength, similar to the observations of Gerding and Johansson [8] in their calorimetric studies of cadmium(II) thiocyanate. Our experimentally determined values of the enthalpy change may therefore be approximately equated with that corresponding to zero ionic strength. The symbol $\Delta H^{\ominus}$ has therefore been used.

Table 4 gives the determined values of ΔG^0 (potentiometric), $\Delta H^{\ominus}$ (calorimetric), and $\Delta S^{\ominus}$ of metal selenocyanato-complexes at 25 °C and compares them with those of thiocyanato-complexes. For comparison, we have taken calorimetric values of $\Delta H^{\ominus}$ of Nancollas and Torrance,[2] our own potentiometric values [1] of ΔG^0, and the resulting $\Delta S^{\ominus}$ values of $[M(SCN)]^+$ complexes. This was done because Nancollas and Torrance [2] did not determine ΔG^0 but used data, mostly spectrophotometric, of different workers in their calculations. For any quantitative comparison it is desirable to use data obtained by the same physical methods. However, the values of ΔG^0 and $\Delta S^{\ominus}$ used by Nancollas and Torrance are given in parentheses.

TABLE 3

Enthalpies of formation, $\Delta H^{\ominus}$, of $[M(SeCN)]^+$ complexes at 25 °C

Metal ion	$10^2[M(ClO_4)_2]/M$	$10^2[K(SeCN)]/M$	q/J	$-\Delta H^{\ominus}/kJ\ mol^{-1}$	
Co^{2+}	2.470	1.007	3.41	6.42	Mean 6.35 ± 0.18
	2.965	1.007	3.90	6.62	
	2.223	1.208	3.67	6.24	
	2.717	1.208	4.09	6.13	
	2.965	1.208	4.44	6.36	
	2.332	1.540	4.89	6.53	
	2.332	1.027	3.20	6.12	
Ni^{2+}	4.632	1.007	7.85	8.23	Mean 8.70 ± 0.50
	5.559	1.007	9.21	8.90	
	3.706	0.604	4.67	8.81	
	4.632	0.604	5.64	9.62	
	3.706	1.007	6.77	7.88	
	5.024	1.027	8.88	8.81	
	5.024	1.540	12.7	8.65	
Cd^{2+}	5.117	1.007	17.6	12.15	Mean 11.1 ± 0.4
	5.117	0.604	10.4	11.76	
	5.117	0.805	12.6	10.77	
	3.411	1.007	13.0	10.36	
	3.411	0.604	8.36	10.80	
	4.752	1.540	23.4	11.19	
	4.752	1.027	15.4	10.72	

TABLE 4

Comparison of thermodynamic functions for selenocyanato- and thiocyanato-complexes at 25 °C. Values given in parentheses are those used by Nancollas and Torrance [2]

	$[M(SCN)]^+$			$[M(SeCN)]^+$		
Metal ion	ΔG°/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}	ΔG^0/kJ mol^{-1}	$\Delta H^{\ominus}$/kJ mol^{-1}	$\Delta S^{\ominus}$/J K^{-1} mol^{-1}
Co^{2+}	-10.7 ± 0.1	-6.82 ± 0.67	12.9 ± 2.6	-8.50 ± 0.29	-6.35 ± 0.18	7.21 ± 1.58
	(-9.82)	(-6.82)	(10.1)			
Ni^{2+}	-11.3 ± 0.1	-9.46 ± 0.33	6.18 ± 1.40	-9.45 ± 0.48	-8.70 ± 0.50	2.52 ± 3.28
	(-10.0)	(-9.46)	(1.91)			
Cd^{2+}	-12.3 ± 0.1	-2.93 ± 0.42	31.3 ± 0.8	-11.3 ± 0.2	-11.1 ± 0.4	0.75 ± 2.20
	(-14.3)	(-2.93)	(38.1)			

Although the thermodynamic parameters, particularly the $\Delta S^{\ominus}$ values, are not as accurate as desirable, some broad and definite conclusions can be drawn from them. The results show that formation of $[Cd(SCN)]^+$ from the respective ions is conspicuously less exothermic but more entropy-favoured ($\Delta S^{\ominus}$ more positive). This complex consists of a mixture of *N*- and *S*-bonded species whereas $[Co(SCN)]^+$ and $[Ni(SCN)]^+$ are *N* bonded.[9] The *S*-

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[8] P. Gerding and B. Johansson, *Acta Chem. Scand.*, 1968, **22**, 2255.

[9] K. A. Taylor, T. V. Long, and R. A. Plane, *J. Chim. phys.*, 1967, **47**(1), 138.

bonded $[Cd(SCN)]^+$ species is non-linear[10-13] (M–S–C angle, <180°) and its formation is sterically less favourable;[10] it is also expected to have a less favourable enthalpy change. However, a more positive entropy change is expected as the formation of a non-linear species liberates more water molecules from the hydration sphere and increases the degree of freedom. Moreover, co-ordination at a S atom, the more probable site of the negative charge[13] of $[SCN]^-$, would result in more effective charge neutralisation and hence a more positive entropy change.[2] Thus the anomalous behaviour of $[Cd(SCN)]^+$ may be due to the existence of *S*-bonded species. The behaviour of $[Cd(SeCN)]^+$ is, however, not similar to that of $[Cd(SCN)]^+$. Our thermodynamic data thus suggest that, unlike $[SCN]^-$, the $[SeCN]^-$ ion most probably co-ordinates with Cd^{2+} ions through the nitrogen atom. It must, however, be pointed out that the above conclusions are tentative and should be substantiated by more conclusive crystallographic and spectroscopic evidence.

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