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STUDIES ON ION ASSOCIATION: THERMODYNAMICS OF THIOCYANATE COMPLEXES OF SOME BIVALENT METAL IONS

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ABSTRACT

Silver–silver thiocyanate electrode has been utilised to determine the free energy changes of the complex formation reactions of monothiocyanato complexes of Mn^{II}, Co^{II}, Ni^{II}, Zn^{II} and Cd^{II} which are shown to be more accurate than the previously determined values. The enthalpy and entropy changes have been calculated from the temperature coefficient of K. It is shown that the complexes are of inner-sphere type with bonding through the nitrogen atom. The crystal field stabilisation energies have also been calculated from the enthalpy changes.

INTRODUCTION

A survey of literature shows that association equilibria involving bivalent metal ions and thiocyanate have been investigated. Most of the papers report the stability constant of $MSCN^+$ species at high ionic strength. Only a few works[1–5] have been devoted to the determination of thermodynamic dissociation constant of monothiocyanato complexes by spectrophotometry. Nancollas and Torrance[6] have evaluated the thermodynamic functions (ΔG^0, ΔH^0 and ΔH^0) for the formation of monothiocyanato complexes of bivalent metal ions. Silver–silver thiocyanate electrode has recently been developed and can suitably be used to make accurate studies of equilibria involving SCN^- ions. In this paper, we report thermodynamic instability constants of monothiocyanato complexes of Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} determined potentiometrically using the above electrode and in some cases the results have been checked by spectrophotometric method. The thermodynamic functions (ΔG^0, ΔH^0 and ΔS^0) for the complex formation reactions have been estimated from the temperature coefficient of K.

EXPERIMENTAL

Preparation and estimation of solutions

Stock solutions of metal perchlorates were prepared by adding excess of metal carbonates (E. Merck, G. R.) to dilute perchloric acid (E. Merck, G. R.) solution, digesting the contents in a steam bath for several hours, allowing to stand for a few days and subsequently filtering to get clear solutions. The metal contents were estimated by standard methods. Potassium thiocyanate (E. Merck, G. R.) was estimated volumetrically by Volhard's method. All other chemicals were of "Analytical Grade". Solutions were prepared in triply distilled water.

Potentiometric method

Silver–silver thiocyanate electrode was prepared by the method of Prasad *et al.*[7] improved upon by Vanderzee and Smith[8]. A concentration cell of type

$$\begin{array}{l|l||l||l|l} & \text{I} & & \text{II} & \\ \text{Ag, AgSCN(s)} & \text{KSCN(aq.)}(c_1) & \text{Saturated} & \text{KSCN(aq.)}(c_1) & \text{AgSCN(s)Ag} \\ & & NH_4NO_3 & Mn(ClO_4)_2\text{(aq.)}(c_2) & \end{array}$$

was set up. The electrodes were prepared in sets of 10–15 at a time and allowed to equilibrate in 0.1 *M* solution of KSCN for 48–72 h. Only those pairs in which the potential difference did not exceed 0.2 mV were used. Saturated ammonium nitrate as bridge solution was found to be very suitable and reduces the liquid junction potential to a negligible value (<0.2 mV). Cells were set up inside air thermostats within 0.1 °C accuracy. The EMF of the cell is given by

$$E = \frac{2.303RT}{F} \log \frac{a_{SCN^-}\,(\text{I})}{a_{SCN^-}\,(\text{II})}$$

Calculations of thermodynamic instability constants were similar to our previous paper[9] assuming the ionic equilibria as

$$\begin{array}{lll} M(SCN)_2 \rightleftharpoons & MSCN^+ & + SCN^- \\ & (1-\beta)\alpha c & \alpha c \\ & \downarrow\uparrow & \\ & M^{2+} & + SCN^- \\ & \alpha\beta c & \alpha\beta c \end{array}$$

At the concentrations used where $[M^{2+}] > [SCN^-]$, α is found to be equal to 1. The instability constant of $MSCN^+$ species is given by

$$K_{MSCN^+} = \frac{[M^{2+}]\,[SCN^-]}{[MSCN^+]} \times f_{2^+}$$

assuming $f_{SCN^-} = f_{MSCN^+}$. The activity coefficients for the reacting species were calculated with the help of Davies[10] equation from the ionic strengths calculated by the methods of successive approximations[9].

Spectrophotometric method

To check the reliability of our potentiometric results we determined the instability constants in a few systems (Cd^{2+} and Co^{2+}) by spectrophotometry. The changes of absorbancy of thiocyanate at 250 mμ by cadmium perchlorate and that of cobalt perchlorate at 510 $m\mu$ by potassium thiocyanate were used to calculate the instability constants. To a fixed concentration of the absorbing reactant the transparent reactant of varying concentration was added and the optical density measured. Assuming $[M(SCN)_2]=0$ at our concentration conditions, calculations were done with the familiar equation[9].

$$\frac{c_1}{d_2-d_1} = \frac{1}{\varepsilon_2-\varepsilon_1} + \frac{K_{\text{inst}}}{(\varepsilon_2-\varepsilon_1)l} \cdot \frac{1}{(c_2-x)f_{2^+}}$$

where,

c_1 = concentration of the absorbing reactant,
c_2 = concentration of the transparent reactant,
d_1 = absorbancy of the absorbing reactant solution,
d_2 = absorbancy of the mixed solution,
ε_1 = extinction coefficient of the absorbing reactant,
ε_2 = extinction coefficient of the complex species, and
x = concentration of the complex.

After a series of successive approximations and refinements as detailed in reference 9, the slope and intercept of

$$\frac{c_1}{d_2-d_1} \text{ vs. } \frac{1}{(c_2-x)f_{2^+}}$$

plot gave K_{inst}.

RESULTS AND DISCUSSION

Table I gives the determined values of thermodynamic K_{inst} for the monothiocyanato complexes at different temperatures. The satisfactory agreement between the potentiometric and spectrophotometric results in $CoSCN^+$ and $CdSCN^+$ complexes support the accuracy and reliability of our data.

Table II gives the thermodynamic instability constants of monothiocyanato complexes at 25°C reported in the literature. A comparison of our results with those given in Table II show a discrepancy in the case of Zn and Cd. However, Tur'yan and Serova[11] reported a value of 1.82×10^{-2} for the instability constant of $CdSCN^+$ species at 25°C and 0.1 M potassium nitrate. When correction is made for ionic strength, the instability constant of $CdSCN^+$ turns out to be 6.37×10^{-3} which compares well with our data at 25°C. Although, Irving–Williams order[12] for the stability of monothiocyanato complexes is reflected in our results, $ZnSCN^+$ is found to be less stable than $CoSCN^+$ and $NiSCN^+$ in contrast to the results in Table II where the sequence Zn > Ni > Co for the stabilities is maintained. However, a survey of literature[13] shows that the sequence Ni > Co > Zn (same as our observed sequence) holds good for most ligands which form complexes with the concerned metal ions. In view of this our value of K_{inst} for $ZnSCN^+$ seems justified.

TABLE I

THERMODYNAMIC INSTABILITY CONSTANTS OF MONOTHIOCYANATO COMPLEXES

System	*No. of reading taken*	*Temperature* (± 0.1 °C)	K_{inst} $\times 10^2$	*Method*
$MnSCN^+ \rightleftharpoons Mn^{2+} + SCN^-$	6	25	(7.02±0.50)	Potentiometry
	6	35	(8.58±0.55)	Potentiometry
	6	45	(10.34±0.62)	Potentiometry
$CoSCN^+ \rightleftharpoons Co^{2+} + SCN^-$	7	25	(1.36±0.04)	Potentiometry
	7	35	(1.67±0.03)	Potentiometry
	7	45	(2.17±0.07)	Potentiometry
	10	27	(1.32±0.20)	Spectrophotometry (510mμ)
$NiSCN^+ \rightleftharpoons Ni^{2+} + SCN^-$	8	25	(1.05±0.04)	Potentiometry
	8	35	(1.40±0.04)	Potentiometry
	8	45	(1.81±0.06)	Potentiometry
$ZnSCN^+ \rightleftharpoons Zn^{2+} + SCN^-$	6	25	(3.22±0.18)	Potentiometry
	6	35	(3.79±0.12)	Potentiometry
	6	45	(4.28±0.13)	Potentiometry
$CdSCN^+ \rightleftharpoons Cd^{2+} + SCN^-$	7	25	(0.71±0.03)	Potentiometry
	8	35	(0.85±0.02)	Potentiometry
	7	45	(1.02±0.03)	Potentiometry
	10	30	(0.78±0.02)	Spectrophotometry (250 mμ)

TABLE II

THERMODYNAMIC INSTABILITY CONSTANT OF MONOTHIOCYANATO COMPLEXES AT 25 °C REPORTED IN THE LITERATURE

	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
K_{inst}	5.9×10^{-2}	1.9×10^{-2}	1.73×10^{-2}	4.70×10^{-3}	1.40×10^{-2}	3.11×10^{-3}
Reference	1	2	2	2	3	4

Table III gives our determined values for the thermodynamic functions (ΔG^0, ΔH^0 and ΔS^0) of the formation reactions at 25 °C and compares with the values of Nancollas and Torrance[6] determined calorimetrically. The ΔH^0 values calculated from temperature coefficient of K (our work) and by calorimetry[6] differ within 3 kcal, which is the order of magnitude of difference often observed between the two methods. Recently, Izaat, Eatough, Christensen and Bartholomew[16] have determined the ΔH^0 of formation of monosulphato complexes of various bi- and trivalent metal ions calorimetrically and compared with different reported values in the literature from the temperature coefficient of K. Such difference in the magnitude of the thermodynamic quantities as existing between our data and that of Nancollas *et al.*[6] is also seen in the sulphato complexes and the temperature coefficient data show higher values of ΔH^0 in most cases. Nancollas and Torrance[6] data suffer from one criticism in that they used $-\Delta G^0$ values of different workers. In their work the reactants were mixed and heat change measured. The concentration of the complex formed in the mixture was calculated from the initial concentrations of the reactants and the available data for K. It is desirable to determine K(*i.e.*, $-\Delta G^0$) along with the heat changes in the calorimeter. An approximate idea of the uncertainty of Nancollas data can be had from the following example. The $-\Delta H^0$ value of $CdSCN^+$ calculated from Nancollas calorimetric reading using our value of K is ~0.9 kcal.mole^{-1}. This is about 30% higher than the value of (0.7±0.1) kcal.mole^{-1}, calculated by Nancollas using the value of K from the previous literature. Similar uncertainties may exist with the ΔH^0 values of other complexes also.

TABLE III

THERMODYNAMIC DATA FOR COMPLEX FORMATION REACTION AT 25°C $M^{2+}+SCN^- \rightleftharpoons MSCN^+$

Metal ion	$-\Delta G^0$ (*kcal/mole*)		$-\Delta H^0$ (*kcal/mole*)		$G^0_{M^{2+}(aq.)}$[c]
	Our result[a]	*Value used by Nancollas and Torrance*[b]	*Our result*	*Nancollas and Torrance result*	
Mn^{2+}	1.57±0.04	1.68±0.06	3.29±0.04	0.92±0.18	−54.40
Co^{2+}	2.55±0.02	2.35±0.03	4.45±0.46	1.63±0.16	−12.80
Ni^{2+}	2.70±0.02	2.40±0.02	5.15±0.52	2.26±0.08	−11.53
Cu^{2+}	—	3.18±0.01	—	3.00±0.15	15.53
Zn^{2+}	2.04±0.03	2.53±0.02	2.67±0.55	−0.22±0.20	−35.18
Cd^{2+}	2.93±0.03	3.42±0.01	3.43±0.49	0.70±0.10	−18.58

[a] Our values of $-\Delta G^0$ at 25°C were calculated from potentiometric data. [b] Nancollas and Torrance did not determine $-\Delta G^0$ but used data available in literature. [c] $G^0_{M^{2+}(aq.)}$ values are collected from Ref. 15 except for Mn^{2+} which is taken from Ref. 14. Values reported in both the references agree very well.

Nature of binding between metal and ligand

Irving–Williams order[12] of stability of $MSCN^+$ species and the calculated distance of closest approach between the metal ion and SCN^- ions in Co^{II}, Ni^{II}, Cu^{II}, Mn^{II} and Zn^{II} calculated by Williams[2] indicate that the interaction between the metal and SCN^- ions result in the formation of innersphere complex species (not ion-pairs in which at least one solvent molecule is interposed between the associate ions) as the major product. This finds further support from the Raman intensity study of Taylor, Long and Plane[17]. The standard free energy change ($-\Delta G^0$) of the reaction

$$M^{2+}(aq.)+SCN^-(aq.) \rightleftharpoons MSCN^+(aq.)$$

is given by the expression

$$\Delta G^0 = G^0_{\mathrm{MSCN^+(aq.)}} - G^0_{\mathrm{M^{2+}(aq.)}} - G^0_{\mathrm{SCN^-(aq.)}}$$

Duncan and Kepert[18] have suggested that the plot of $-\Delta G^0$ *vs.* $G^0_{\mathrm{M(aq.)}}$ will be a straight line with a positive slope for inner-sphere complexes of different metal ions with a particular ligand. We have plotted (Fig. 1) the same with our free energy data

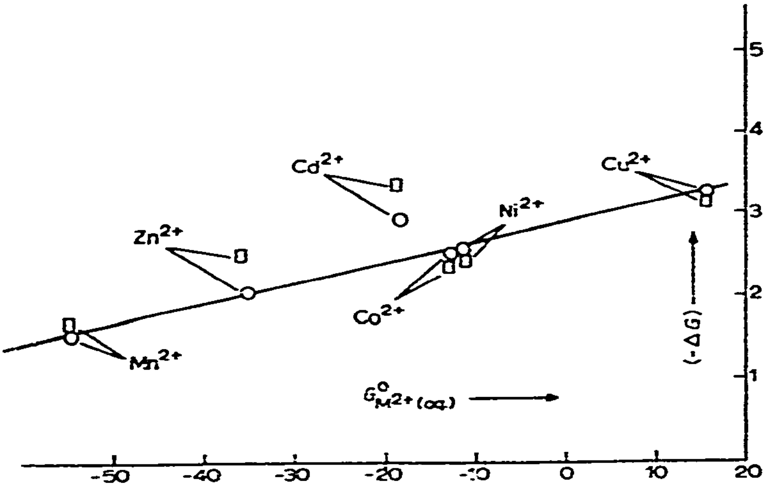

Fig. 1. Plot of $-\Delta G^0$ *vs.* $G^0_{\mathrm{M(aq.)}}$ for complexes of different metal ions with SCN^-. ⊙, our data, ⊡, data used by Nancollas *et al.*

and that used by Nancollas *et al.*[6] It can be seen that our points fit to a better straight line further establishing the correctness of our free energy data. The only point in the plot which slightly deviates from the straight line is that of Cd which is understandable because of the ambidentate nature of $CdSCN^+$ (*i.e.*, complex formation takes place both through N and S atoms whereas in the case of other metal ions in this series the bonding is always through N atom[17]).

Swift and Connick[19] interpreted the rate of water exchange from the primary solvation spheres of hexaquo metal ions in terms of crystal field effects. They also found that a nearly good linear correlation is satisfied between the stability constants of monoethylene diamine complexes of the metal ions (Fe^{2+}, Mn^{2+}, Co^{2+} Ni^{2+} and Cu^{2+}) which are known to be inner-sphere types and their water-exchange rate constants. The deviation observed in the case of $Co(OH_2)_6^{2+}$ is explained by them as due to the existence of $(Co(OH_2)_6^{2+}$ as a slightly distorted octahedral entity at the room temperature. Interestingly similar plot (log*K* *vs.* log$k_1$$H_2O$) for monothiocyanato complexes (Fig. 2) is found to be linear indicating inner-sphere binding of the SCN^- to the metal ion considered. A similar deviation is also observed for cobalt system.

Calculation of ligand-field stabilisation energy

According to George and McClure[20] the transition series contraction energy E_r (Mn–Zn) for the formation of monothiocyanato complexes ($MSCN^+$) can be defined as the negative heat of reaction:

$$Zn^{2+}(g) + MnSCN^{+}(aq.) \rightarrow ZnSCN^{+}(aq.) + Mn^{2+}(g)$$

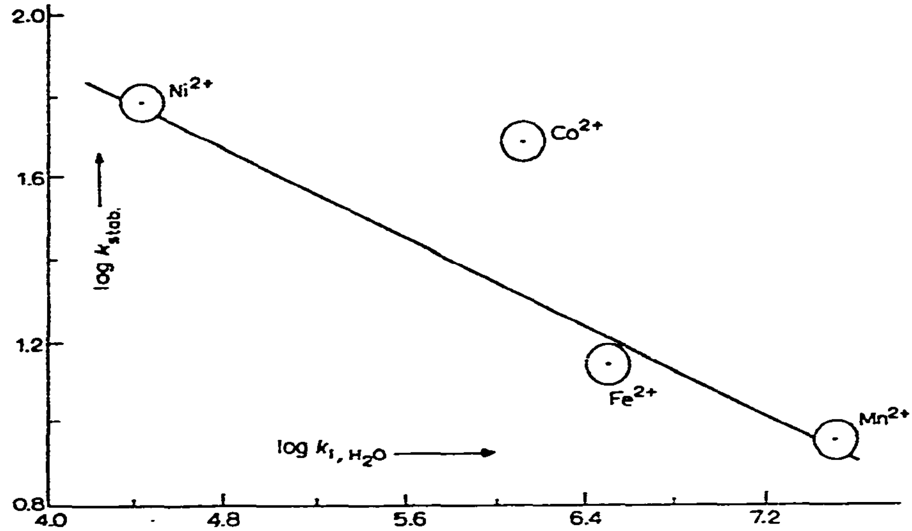

Fig. 2. Plot of log K vs. log k_1,H_2O for monothiocyanato complexes.

which can be calculated from the relationship

$$E_r = -[\Delta H_{H(Zn^{2+})} + \Delta H_{C(Zn^{2+})}] + [\Delta H_{H(Mn^{2+})} + \Delta H_{C(Mn^{2+})}],$$

where $\Delta H_{C(M^{2+})}$ is the heat of the complex formation as shown in the equation

$$M^{2+}(aq.) + SCN^{-}(aq.) \xrightarrow{\Delta H_C} MSCN^{+}(aq.)$$

and $\Delta H_{H(M^{2+})}$ is the heat of hydration of the transitional metal ion M^{2+} (as given by George and McClure[20])

$$M^{2+}(g) \xrightarrow{\Delta H_H} M^{2+}(aq.)$$

The ligand-field stabilisation energy, δH, in the monothiocyanato complexes of the first row transition metal ions can be obtained from the enthalpy changes by the equation

$$\delta H_{(M^{2+})} = [\Delta H_{C(Mn^{2+})} + \Delta H_{H(Mn^{2+})}] - [\Delta H_{C(M^{2+})} + \Delta H_{H(M^{2+})}] - \frac{(n-5)}{5} E_r$$

where n = number of d-electrons in the metal ion M^{2+}.

We have calculated δH from the enthalpy data of Nancollas and Torrence[6] and that of ours. The results agree extremely well as can be seen in Table IV.

The calculated δH values compare very well with the δH values for other nitrogen ligands where the bonding is through one N atom[20] ($\delta H_{Co} \approx 26$ kcal.mole^{-1}, $\delta H_{Ni} \approx 36$ kcal.mole^{-1} and $\delta H_{Cu} \approx 30$ kcal.mole^{-1}). This indicates the bond between these metal ions and SCN^- to be through N atom.

TABLE IV

CALCULATION OF LIGAND FIELD STABILISATION ENERGY (δH)

(E_r = 45.97 kcal.mole^{-1} from Nancollas data and 46.49 kcal.mole^{-1} from our data)

	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Number of *d*-electrons	5	7	8	9	10
δH from Nancollas data (in kcal.mole^{-1})	0	25.3	35.8	28.2	0
δH from our data (in kcal.mole^{-1})	0	25.6	36.0	—	0

REFERENCES

1 K. B. Yatsimirskii and V. D. Korableva, *Zhur. Neorg. Khim.*, 3 (1958) 339.
2 T. Williams, *J. Inorg. Nucl. Chem.*, 24, (1962) 1215.
3 K. B. Yatsimirskii and V. D. Tetyushkina, *Zhur. Neorg. Khim.*, 2 (1957) 320.
4 V. P. Vasi'lev and P. S. Mukhina, *Zhur. Neorg. Khim.*, 8 (1963) 1895.
5 R. C. Das, Ph. D. Thesis, Utkal Univ. (India), 1964.
6 G. H. Nancollas and K. Torrance, *Inorg. Chem.*, 6 (1967) 1567.
7 R. N. Parida, S. Aditya and B. Prasad, *J. Ind. Chem. Soc.*, 29 (1952) 377.
8 C. E. Vanderzee and W. E. Smith, *J. Amer. Chem. Soc.*, 78 (1956) 721.
9 R. C. Das, A. C. Dash and J. P. Mishra, *J. Inorg. Nucl. Chem.*, 30 (1968) 2417.
10 C. W. Davies, *J. Chem. Soc.*, (1938) 2093.
11 Ya. I. Tur'yan and G. F. Serova, *Zhur. Neorg. Khim.*, 2 (1957) 336.
12 H. Irving and R. J. P. Williams, *Nature*, (1948) 162, 746; *J. Chem. Soc.*, (1953) 3192.
13 *Stability Constants*, Part I, The Chemical Society, London, 1956.
14 W. A. Latimer, *Oxidation Potentials*, Prentice Hall, London, 1952.
15 J. W. Larson, P. Cerutti, H. K. Gaber and L. G. Hepler, *J. Phys. Chem.*, 72 (1968) 2902.
16 R. M. Izatt, D. Eatough, J. J. Christensen and C. H. Bartholomew, *J. Chem. Soc.* (*A*), (1969) 47.
17 K. A. Taylor, T. V. Long and R. A. Plane, *J. Chim. Phys.*, 47 (1) (1967) 138.
18 J. F. Duncan and D. L. Kepert, in W. J. Hamer (Ed.), *The Structure of Electrolytic Solutions*, Wiley, New York, 1959.
19 T. J. Swift and R. E. Connick, *J. Chem. Phys.*, 37 (1962) 307.
20 P. George and D. S. McClure, in F. A. Cotton (Ed.), *Progress in Inorganic Chemistry*, Vol. 1, Interscience, New York, 1959, p. 381.