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Thermodynamics of Ion Association.[1a] XIV. Metal Monothiocyanate Complexes

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A sensitive differential calorimeter has been used to measure the enthalpies of formation of the monothiocyanate complexes of the divalent cations manganese, cobalt, nickel, copper, zinc, cadmium, and lead at low concentrations in aqueous solution and at 25°. The data have been corrected to zero ionic strength and thermodynamic functions ΔG, ΔH, and ΔS have been evaluated for the reactions $M^{2+} + CNS^- \rightleftharpoons MCNS^+$, together with the hydration entropies of the complex species. The values are discussed in terms of the properties of the metal ions and possible linkage isomerism involving the anion.

A number of metal monothiocyanate complexes have been characterized by the determination of stability constants at a single temperature but no calorimetric measurements have hitherto been made of the heats of association. The thiocyanate ion is of special interest since it exhibits linkage isomerism, bonding to the metal ion either through its sulfur or nitrogen atom.[2] In addition, there is some doubt as to the linearity of the metal–thiocyanate bonds and it has been suggested that the steric requirements of M–SCN bonding are greater than for M–NCS.[3] The latter is usually linear whereas the M–S–C in M–SCN is nonlinear.[4]

Although the monothiocyanate complexes of the bivalent transition metals are rather weak, it is possible, by means of sensitive calorimetric techniques, to measure the heats of association with some degree of accuracy. In the present study, experimental conditions were chosen such that only the 1:1 complexes were present, and measurements were made at low concentrations so that activity coefficients could be calculated.

Experimental Section

Preparation of Materials.—Grade A glassware and AR reagents were used throughout. Manganese and nickel perchlorate solutions were prepared by dissolving the freshly precipitated carbonates in perchloric acid and analyzed on a column of cation-exchange resin (Amberlite IR-120) in the hydrogen form. Cobalt(II) perchlorate was crystallized by the addition of excess perchloric acid to the chloride and purified by recrystallization. The cation content was determined by complexometric titration with EDTA.[5] Copper(II) and zinc perchlorate solutions were made by dissolving the oxides in perchloric acid; analysis for copper ion was made by thiosulfate titration and for zinc ion by complexometric titration.[5] Lead perchlorate solutions were prepared from the nitrate and perchloric acid[6] and analyzed for lead by complexometric titration.[5]

Calorimetric Experiments.—The calorimeter and experimental technique have been described previously.[7,8] Temperature changes were measured on dilution of small volumes of ammonium thiocyanate solutions with an approximately 30 times greater volume of the metal ion solutions of the same ionic strength. Blank experiments were carried out in order to determine the heats of dilution, under the same conditions, of small volumes of ammonium thiocyanate into solutions of the same ionic strength but containing no metal ion. The ionic strength was always less than 6.3×10^{-2} *M* and concentrations were chosen such that only $MCNS^+$ was formed in the calorimeters.

Results and Discussion

The concentrations of ionic species in the solutions may be calculated from equations for the total ligand concentration

$$m_1 = [MCNS^+] + [CNS^-]$$

for the total metal ion concentration

$$m_2 = [MCNS^+] + [M^{2+}]$$

and for the association constant

$$K = \frac{[MCNS^+]}{[M^{2+}][CNS^-]f_2}$$

Combining these equations gives a quadratic in $[MCNS^+]$

$$Kf_2[MCNS^+]^2 - \{1 + (m_1 + m_2)Kf_2\}[MCNS^+] + m_1m_2Kf_2 = 0$$

which may be solved on an electronic computer by successive approximations for I ($= m_1 + m_2 + 2[M^{2+}]$), the ionic strength. Activity coefficients were calculated from the Davies equation[9] and the values of the association constants, K, used in the computations were the reported spectrophotometric values shown in Table I.[10–14] The results of the calorimetric experiments are summarized in Table II, in which ΔH_i is the heat change per mole of complex and ΔH_0 the heat of association corrected to zero ionic strength.[15] The actual enthalpy values are, of course, somewhat de-

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TABLE I

ASSOCIATION CONSTANTS FOR METAL MONOTHIOCYANATES

	Metal ion						
	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
K, M^{-1}	17.0	52.3	57.8	212.7	71.4	322.0	12.4
Ref	10	11	11	11	12	13	14

TABLE II

CALORIMETRIC RESULTS AT 25°

10^3m_1, M	10^3m_2, M	$10^4[MCNS^+]$, M	10^2I, M	$-\Delta H_i$, kcal $mole^{-1}$	$-\Delta H_0$, kcal $mole^{-1}$
		Manganese Thiocyanate			
5.954	12.002	5.03	4.095	1.23	0.95
5.954	12.001	5.03	4.095	1.21	0.94
6.092	9.823	4.44	3.457	1.06	0.80
6.464	10.423	4.91	3.675	1.04	0.78
3.697	9.936	2.82	3.294	1.40	1.15
Mean $\Delta H_0 = -0.92 \pm 0.11$ kcal $mole^{-1}$					
		Cobalt Thiocyanate			
3.605	5.545	4.71	2.068	1.87	1.66
4.092	6.294	5.78	2.339	1.93	1.72
3.580	5.507	4.66	2.054	1.86	1.66
4.268	6.566	6.18	2.436	1.72	1.52
Mean $\Delta H_0 = -1.63 \pm 0.16$ kcal $mole^{-1}$					
		Nickel Thiocyanate			
3.726	7.688	6.35	3.259	2.51	2.26
4.314	8.901	7.97	3.761	2.40	2.15
2.445	5.044	3.15	2.468	2.59	2.37
4.191	8.648	7.62	3.656	2.51	2.25
Mean $\Delta H_0 = -2.26 \pm 0.08$ kcal $mole^{-1}$					
		Copper Thiocyanate			
4.019	6.710	14.75	2.883	3.16	2.92
3.918	6.540	14.23	2.813	3.08	2.84
2.544	4.248	7.47	2.814	3.27	3.06
2.371	3.959	6.74	2.040	3.35	3.14
Mean $\Delta H_0 = -2.99 \pm 0.15$ kcal $mole^{-1}$					
		Zinc Thiocyanate			
2.988	5.448	4.79	2.546	0.00 ± 0.20	−0.22 ± 0.20
3.789	6.909	7.03	3.030	0.00 ± 0.20	−0.23 ± 0.20
3.742	5.457	5.89	2.604	0.00 ± 0.20	−0.22 ± 0.20
Mean $\Delta H_0 = 0.22 \pm 0.20$ kcal $mole^{-1}$					
		Cadmium Thiocyanate			
5.170	8.652	26.38	2.585	0.91	0.69
5.122	8.573	26.07	2.563	1.04	0.84
3.693	8.241	19.40	2.454	0.93	0.68
3.757	8.384	19.84	2.494	0.87	0.66
5.011	16.774	33.15	4.870	0.96	0.68
5.034	16.850	33.33	4.892	0.88	0.59
Mean $\Delta H_0 = -0.69 \pm 0.10$ kcal $mole^{-1}$					
		Lead Thiocyanate			
4.929	10.048	2.80	3.451	0.00 ± 0.20	−0.25 ± 0.20
4.943	10.076	2.81	3.461	0.00 ± 0.20	−0.25 ± 0.20
5.876	19.165	5.16	6.234	0.00 ± 0.10	−0.32 ± 0.10
5.867	19.136	5.15	6.225	0.00 ± 0.10	−0.32 ± 0.10
5.919	19.305	5.22	6.279	0.00 ± 0.10	−0.32 ± 0.10
5.849	19.079	5.13	6.206	0.00 ± 0.10	−0.32 ± 0.10
Mean $\Delta H_0 = 0.30 \pm 0.20$ kcal $mole^{-1}$					

pendent upon the equation used to evaluate the activity coefficients. The justification for using the Davies equation[9] is its satisfactory interpretation of the results of many other associating systems.[8] The calculated thermodynamic functions are given in Table III together with estimated uncertainties. There are few data available for direct comparison with the results of the present work. Mohapatra[16] reported values for nickel monothiocyanate of $\Delta H = -13.17$ kcal $mole^{-1}$ and $\Delta S = -37.0$ cal deg^{-1} $mole^{-1}$ calculated from measured K values at 25 and 35°. It seems most unlikely that such a low entropy is correct for an association reaction involving charged species. A similar temperature coefficient study on lead monothiocya-

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[16] P. P. Mohapatra, *J. Indian Chem. Soc.*, **38**, 845 (1961). The value actually given in this reference, $\Delta S = +51.1$ cal deg^{-1} $mole^{-1}$, was miscalculated.

TABLE III
THERMODYNAMIC FUNCTIONS FOR METAL COMPLEX FORMATION

Reaction	$-\Delta G°$, kcal mole^{-1}	$-\Delta H°$, kcal mole^{-1}	$\Delta S°$, cal deg^{-1} mole^{-1}	$\Delta S°_{hyd}(MCNS^+)$, cal deg^{-1} mole^{-1}
$Mn^{2+} + CNS^-$	1.68 ± 0.06	0.92 ± 0.18	2.5 ± 0.8	−76
$Co^{2+} + CNS^-$	2.35 ± 0.03	1.63 ± 0.16	2.2 ± 0.8	−82
$Ni^{2+} + CNS^-$	2.40 ± 0.02	2.26 ± 0.08	0.5 ± 0.4	−87
$Cu^{2+} + CNS^-$	3.18 ± 0.01	3.00 ± 0.15	0.6 ± 0.5	−82
$Zn^{2+} + CNS^-$	2.53 ± 0.02	−0.22 ± 0.20	9.2 ± 0.8	−75
$Cd^{2+} + CNS^-$	3.42 ± 0.01	0.70 ± 0.10	9.2 ± 0.4	−64
$Pb^{2+} + CNS^-$	1.49 ± 0.06	−0.30 ± 0.20	6.0 ± 1.0	−48

nate[14] led to an exothermic $\Delta H = -0.6$ kcal mole^{-1} whereas the value found in this work was endothermic. These discrepancies illustrate the inaccuracies which can arise in the calculation of enthalpies from a limited study of association constants.

The heats of formation of the transition metal complexes increase from manganese to copper and there is a fall to zinc. This order is generally followed when the metal–ligand bond is predominantly covalent, and it parallels the variation of the second ionization potential for the metal ion. The corresponding entropy changes are small as would be expected for the formation of a charged complex which will retain some of its solvent-ordering properties. Hydration entropies of the complexes, given in Table III, were calculated from

$$\Delta S°_{hyd}(MCNS^+) = \Delta S° - S°_g(MCNS^+) + S°(M^{2+}) + S°(CNS^-)$$

in which

$$S°_g(MCNS^+) = S°_{trans}(MCNS^+) + S°_{rot}(MCNS^+)$$

was obtained, as described previously,[17] by assuming a linear structure for the complex species. Any deviation from linearity would have little effect on the gas entropy values calculated. $\Delta S°_{hyd}$ values refer to standard states of 1 M gas ions and 1 m aqueous ions; the entropies of the aqueous ions were the tabulated values.[18,19]

The abnormally endothermic enthalpy and large positive entropy changes for the formation of the zinc monothiocyanate complex may reflect the elimination of extra water molecules from the cosphere of this small cation. Back-coordination to the thiocyanate ion from the filled shell of the zinc ion may result in a more bent complex requiring, for its formation, the removal of more than one water molecule from the hydration sphere of the cation.

With the exception of cadmium and lead, all of the metal ions in Table II will be expected to be coordinated through the N atom. Coordination involving the S atom, the most probable site of the negative charge,[20] will result in a more effective neutralization of charge in the formation of the complex and a more positive ΔS. The class b ions of cadmium and lead will be expected to show some bonding through the sulfur atom, and it is seen that their complexes are formed with abnormally large and positive entropy changes as compared with the other metal ions studied.

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