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Note

THERMODYNAMIC STUDIES OF SOME COMPLEXES OF 2-MERCAPTOPHENYL-4-BENZAMIDOTHIOSEMICARBAZIDE

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The stability constants (log K) of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) complexes with 2-mercaptophenyl-4-benzamidothiosemicarbazide were found to be proportional to the ionic strength and inversely proportional to temperature. Plots of thermodynamic stability constant at zero ionic strength (log $K^{\ominus}$) vs. T^{-1} gave linear curves which predicted a temperature independent heat of association of the reaction and zero values of $\Delta C_p^{\ominus}$. The negative values of $\Delta G^{\ominus}$ and $\Delta H^{\ominus}$ showed exothermic metal–ligand interaction. Sufficiently large positive values of $\Delta S^{\ominus}$ further supported the spontaneous formation of stable complexes.

In continuation of our earlier thermodynamic studies [1] of the complexes of benzamidothiosemicarbazide with some divalent metal ions, we present a summary of the thermodynamic stability constants and thermodynamic parameters of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) complexes of 2-mercaptophenyl-4-benzamidothiosemicarbazide (SH-BTSC).

EXPERIMENTAL

2-Mercaptophenyl-4-benzamidothiosemicarbazide was prepared as described by Verma [2] (S found; 25.98%; S calculated; 26.46%). A solution of SH-BTSC was prepared in an 80:20 ethanol–water (v/v) mixture. Fresh solution was always used. Stock solutions of metal chlorides of K(I), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Hg(II) and metal acetates of Zn(II), Cd(II) and Pb(II) were prepared in double distilled CO_2-free water and their strengths were determined by the recommended methods. All the reagents were of AnalaR grade.

The following mixtures of solutions (total volume 30 ml in each case) were titrated against carbonate-free 0.1 N KOH at various temperatures (20, 25, 30 and 35 ± 0.1°C) using a Toshniwal pH meter (model CL 49) with a combined glass and saturated calomel electrode: (i) 20 ml of 0.02 M

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TABLE 1

Values of thermodynamic stability constants at different temperatures

Complex	log $K^{\ominus}$ at different temperature			
	20 °C	25 °C	30 °C	35 °C
Mn–L	10.35	10.18	10.07	9.94
Fe–L	14.11	13.89	13.65	13.49
Co–L	10.48	10.36	10.25	10.15
Ni–L	10.98	10.86	10.77	10.59
Cu–L	13.06	12.92	12.81	12.63
Zn–L	10.81	10.67	10.56	10.40
Cd–L	9.67	9.53	9.48	9.36
Hg–L	11.64	11.48	11.28	11.09
Pb–L	8.52	8.46	8.36	8.25

L is deprotonated SH-BTSC ($C_8H_8N_4OS_2$).

SH-BTSC + X ml of 2.0 M KCl, (ii) 20 ml of 0.02 M SH-BTSC + X ml of 2.0 M KCl + Y ml of 0.02 M metal salt solution ($X = 1$, 2 and 3 ml; $Y = 1$, 1.5 and 2 ml). The observed pH measurements were corrected for mixed solvents according to the method of Van Uitert and Hass [3].

For each metal–ligand system pH titration of BTSC + KCl alone and in the presence of different concentrations of metal ions at different ionic strengths (0.067, 0.133 and 0.20 mol dm^{-3} KCl) and temperatures (20, 25, 30 and 35 °C) were performed according to the method of Calvin and Melchior [4]. From the titration curves, at different pH values, different sets of $\bar{n}$ values were determined and the corresponding concentration of free ligand ($\overline{L}^-$) was calculated. Normal formation curves were obtained for all the metals. The values of pK at $\bar{n} = 0.5$ gave the overall stability constants. At each temperature average values of log K were then plotted against ionic strength for each metal–ligand system and the curves were extrapolated to zero ionic strength to give thermodynamic stability constants, log $K^{\ominus}$ (Table 1).

For each metal–ligand system at the stated temperature, log $K^{\ominus}$ values were plotted against T^{-1}. To calculate the heat of association the method of least squares was applied to the plots [5,6] of log $K^{\ominus}$ vs. T^{-1} to obtain a linear fit with a slope of $-\Delta H^{\ominus}/R$. By graphical extrapolation of the curves an intercept of $\Delta S^{\ominus}/R$ at $1/T = 0$ was obtained. Moreover, the changes in free energy for each metal–ligand were calculated from the equation $\Delta G^{\ominus} = -2.303RT \log K^{\ominus}$.

RESULTS AND DISCUSSION

The pH titration curves of metal–ligand mixtures and of ligand separately showed a lowering of pH indicating the release of protons. Moreover, a

TABLE 2

Thermodynamic parameters of the complexes

System	$-\Delta G^{\ominus}_{25}$ (kJ mol^{-1})	$-\Delta H^{\ominus}$ (kJ mol^{-1})	$+\Delta S^{\ominus}$ (J K^{-1} mol^{-1})
Mn complex	58.09	39.61	61.85
Fe complex	79.25	70.05	27.57
Co complex	59.11	38.29	69.89
Ni complex	61.97	42.55	65.10
Cu complex	73.72	52.22	71.80
Zn complex	60.88	51.55	29.68
Cd complex	54.38	40.31	49.21
Hg complex	65.50	58.91	21.44
Pb complex	48.27	30.64	58.59

maximum lowering in the case of 1 : 1 metal–ligand mixtures and the inflection corresponding to 2 mol of KOH indicated the formation of 1 : 1 complexes. Conductometric studies also supported this stoichiometry of the complexes.

No appreciable change in the protonation values of SH-BTSC was observed pH metrically at different ionic strengths; however, the values were found to decrease with increasing temperature ($pK_1 = 7.65$, 7.62, 7.58 and 7.55; $pK_2 = 8.82$, 8.78, 8.76 and 8.73 at 20, 25, 30 and 35 °C, respectively).

Average values of the overall stability constants of the metal complexes were found to be proportional to the ionic strength and inversely proportional to the temperature. In all cases the linear nature of the log $K^{\ominus}$ vs. T^{-1} plots indicated $\Delta C_p^{\ominus}$ values equal to zero and predicted a temperature independent heat of association. The negative values of $\Delta H^{\ominus}$ (Table 2) indicated the exothermic nature of the metal–ligand interaction. The spontaneous formation of the complex and the anionic complexed species of the ligand were further confirmed by the positive values of $\Delta S^{\ominus}$. Sufficiently large negative values of $\Delta G^{\ominus}$ also showed spontaneous formation of the complexes and the values followed the order Cu > Hg > Ni > Zn > Co > Cd > Pb for divalent metal ions. The highest values of the thermodynamic stability constant and hence $\Delta G^{\ominus}$ were found for the Fe(III) complex owing to the large charge on the central metal atom.

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