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THERMODYNAMICS OF THE INTERACTION OF SOME TRANSITION METAL IONS WITH SOME *N*-SUBSTITUTED THIOBARBITURIC ACIDS

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ABSTRACT

Thermodynamic proton–ligand stability constants of thiobarbituric acid (TBA), *N*-methylthiobarbituric acid (MTBA), *N*-phenylthiobarbituric acid (PTBA), *N*-*o*-tolylthiobarbituric acid (*o*-t-TBA), *N*-*m*-tolylthiobarbituric acid (*m*-t-TBA) and *N*-*p*-tolylthiobarbituric acid (*p*-t-TBA) and thermodynamic metal–ligand stability constants of complexes of Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+} and Mn^{2+} with these *N*-substituted thiobarbituric acids have been determined in aqueous medium by potentiometric measurements. The thermodynamic functions ΔG^0, ΔH^0 and ΔS^0, corresponding to the stepwise complexation processes, have been calculated at 31°C. The stepwise complexation is found to be predominantly an enthalpy-driven process.

INTRODUCTION

Studies on the behaviour of the heterocyclic imines and enols are of current interest in biopolymers and in the physical chemistry of drug action. It is desirable that more information is gathered about similar model systems. Thiobarbituric acid containing enolic and imine groups in a benzenoid heterocyclic ring system has been selected as one such model compound. A literature survey indicates that some solid complexes of thiobarbituric acid have been extracted [1–3]. No systematic work on this compound has been undertaken, however, with regard to the evaluation of the stability constants of the complexes with various metal ions. However, bearing this in mind, an attempt has been made to determine the thermodynamic stepwise proton–ligand and metal–ligand stability constants of some bivalent metal ions with thiobarbituric and some of its *N*-substituted acids.

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EXPERIMENTAL

Thiobarbituric acid used was BDH A.R. grade. All the *N*-substituted thiobarbituric acids have been synthesised by the method reported previously [4]. All the acids were used after further purification. The solutions of metal ions were prepared using BDH A.R. grade samples of metal nitrate or sulphate and were standardised by the conventional gravimetric procedures.

The experimental procedure consisted of pH-metric titrations performed using a pre-calibrated expanded-scale pH meter (Elico 821, India) equipped with a glass electrode and a saturated calomel electrode. Titrations were carried out in a sealed water-jacketed vessel at a fixed temperature. The titrating solution was made up of metal ion (0.001 M), ligand (0.01 M) and $HClO_4$ (0.005 M) and the carbonate-free sodium hydroxide was used as titrant. The ionic strength of the titrating solution was maintained at 0.1 M with $NaClO_4$.

The average number of protons ($n_{\bar{H}}$) associated with H_2A, the average number of ligand molecules attached per metal ion (n^-), and the free ligand exponent (pL) were calculated adopting the Irving–Rossotti technique [5]. By applying various computational methods (e.g., interpolation at half n^- values, interpolation at various n^- values, the mid-point slope method, and the correction term method) the stepwise metal–ligand stability constants were determined. The values obtained by different methods are in fair agreement. Bjerrum's half integral method [6] has been applied to evaluate the first protonation constant of these acids. The second protonation constants were calculated graphically using the following equation

$$\mathrm{pH} = \log K_2^{\mathrm{H}} + \log \frac{2 - n_{\bar{H}}}{n_{\bar{H}}}$$

RESULTS AND DISCUSSION

In all metal–ligand titrations, the n^- values steadily increase with pH from < 0.3 to $> 1.5 - \leqslant 2.1$ before precipitation occurs indicating the formaion of 1 : 2 metal–ligand complexes as the highest complexes in these systems. The thermodynamic stepwise protonation constants of acids and stepwise formation constants of the corresponding metal–ligand complexes obtained by applying activity coefficient corrections on the basis of the Davies equation [7] are summarized in Table 1. Formation constants determined as above, were reproducible to 0.04 log unit or less in replicate experiments, while variation in the initial concentration of metal and ligand gave results with a variation of ±0.10 log unit or less.

pK_a and $\log K$ (or $\log K_1K_2$) should be related linearly since the reactions leading to protonation and complexation are similar; this is found in the present study. Plots of pK_a vs. $\log K_1$ (or $\log K_1K_2$) are straight lines with slopes close to unity indicating that the general relation [8] $\log K = mpK_a + C$ is observed.

From Table 1 it is evident that the introduction of methyl and phenyl, and *ortho-*, *meta-* and *para*-tolyl groups in the *N*-position of the thiobarbituric acid molecule has a parallel effect on the proton–ligand and metal–ligand stability constants; e.g., the pK_a order is TBA < MTBA < *o*-t-TBA < *m*-t-TBA < PTBA < *p*-t-TBA and identical to the order of log *K*.

The small variation in pK_a and log *K* values in going from *N*-phenyl to variously oriented *N*-tolyl derivatives indicates that the steric effect of the methyl group cannot be transmitted appreciably to a distant coordination centre. An unmistakable gradation exists, however, albeit small, as shown above. The substituent effects of interactions of the methyl and phenyl groups then operate through the *N*-heterobenzenoid ring and affect the electron demand of the bonding site. The parallel orders of log *K* and pK_a also emphasise the fact that the net electron demand in metal association remains the same as in protonation.

The $\log K_1$ and $\log K_2$ values of the metal–ligand complexes follow the order $Cu^{2+} > Zn^{2+} > Co^{2+} > Fe^{2+} > Ni^{2+} > Mn^{2+}$ irrespective of the substituents. This sequence is in agreement with that found by Irving and Williams [9].

The values of overall stability constants decrease with increasing temperature, as seen from Table 1 indicating that a lower temperature is favourable for the formation of complexes. The values of changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) accompanying complexation reactions have been calculated at 31°C with the help of equations reported previously [10]. The error in ΔH^0 values lies in the range 0.2–0.5 kcal mol^{-1} and that for ΔS^0 is 0.5 cal K^{-1} mol^{-1}.

The negative values of ΔG^0 (Table 1) show that the reaction tends to proceed spontaneously. The negative values of ΔH^0 (Table 1) suggest that the formation of complexes between acids and metals are enthalpy characterized reactions and this also explains the decrease in the value of log *K* with a rise in temperature. In the consecutive complexation process no significant change in the type of bonding is expected, thus exhibiting enthalpy values which are of nearly the same magnitude. This is also because of the large aromatic moiety, phenyl or tolyl. Considering that thiobarbiturates and transition metal cations behave as soft donors and soft acceptors, respectively, only the liberation of ordered solvent molecules from the solvation shell gives a small positive contribution to entropy because for a soft–soft interaction, a very weak solvation shell occurs. The extent of charge neutralization on associating with metal ions in solution, however, is such that a positive entropy change is not predicted, on the other hand restrictions imposed on rotation and vibration of the ligand upon association will produce a considerable loss of entropy. Thus, the complexation of the

TABLE 1

Thermodynamic stability constants at different temperatures, and other thermodynamic functions at 31 °C

Cations	$\log K_1$			$\log K_2$			$-\Delta H^0$(kcal mol^{-1})		$-\Delta S^0$(cal mol^{-1} K^{-1})	
	18 °C	31 °C	42 °C	18 °C	31 °C	42 °C	$-\Delta H_1^0$	$-\Delta H_2^0$	$-\Delta S_1^0$	$-\Delta S_2^0$
Thiobarbituric acid										
H^+	10.55	10.40	10.27	2.10	1.92	1.82				
Cu^{2+}	8.51	7.63	6.93	6.25	5.85	5.45	24.80	13.68	46.80	18.35
Zn^{2+}	7.49	6.74	6.21	5.56	5.14	4.75	20.15	12.31	35.55	17.07
Co^{2+}	6.82	6.14	5.66	5.30	4.94	4.65	15.93	11.40	24.40	15.00
Fe^{2+}	6.56	5.82	5.41	4.72	4.39	4.12	14.22	10.03	20.23	12.99
Ni^{2+}	6.22	5.65	5.23	4.45	4.17	3.92	13.02	9.12	18.98	11.01
Mn^{2+}	5.54	5.11	4.81	4.02	3.75	3.59	9.72	7.27	8.92	6.84
Methylthiobarbituric acid										
H^+	10.64	10.51	10.36	2.15	1.98	1.87				
Cu^{2+}	8.63	7.74	7.02	6.37	5.92	5.54	26.31	14.23	51.25	19.86
Zn^{2+}	7.61	6.85	6.30	5.68	5.24	4.84	21.67	12.76	40.06	18.12
Co^{2+}	6.94	6.24	5.75	5.42	5.04	4.74	17.40	11.69	28.78	15.52
Fe^{2+}	6.68	5.92	5.50	5.00	4.49	4.22	15.72	10.30	24.73	13.45
Ni^{2+}	6.34	5.76	5.32	4.57	4.28	4.01	14.52	9.30	21.51	11.12
Mn^{2+}	5.67	5.23	4.90	4.15	3.87	3.68	10.02	7.36	9.14	6.57
Phenyl thiobarbituric acid										
H^+	10.87	10.82	10.60	2.28	2.11	2.02				
Cu^{2+}	9.26	8.25	7.59	7.02	6.47	6.11	29.64	25.87	59.90	22.79
Zn^{2+}	8.18	7.30	6.68	6.25	5.70	5.22	25.30	14.13	49.96	20.55
Co^{2+}	7.38	6.65	6.13	5.86	5.45	5.12	20.97	12.55	38.72	16.48
Fe^{2+}	7.05	6.32	5.87	5.39	4.89	4.58	19.60	11.12	35.68	14.34
Ni^{2+}	6.78	6.08	5.66	5.02	4.60	4.35	18.22	9.84	32.23	11.44
Mn^{2+}	5.98	5.50	5.18	4.46	4.14	3.96	13.68	7.64	19.90	6.28

m-*Tolyl Thiobarbituric acid*										
H^+	10.79	10.72	10.53	2.24	2.06	1.97				
Cu^{2+}	8.88	8.02	7.26	6.66	6.24	5.78	28.50	15.33	57.23	22.03
Zn^{2+}	8.24	7.19	6.60	6.12	5.59	5.14	23.98	13.66	46.11	19.50
Co^{2+}	7.20	6.49	5.95	5.78	5.25	4.94	20.29	12.27	37.23	16.48
Fe^{2+}	6.85	6.18	5.74	5.19	4.75	4.45	19.74	10.84	36.77	14.04
Ni^{2+}	6.58	5.99	5.50	4.82	4.52	4.19	17.87	9.66	31.11	11.21
Mn^{2+}	5.88	5.44	5.10	4.36	4.08	3.88	12.99	7.55	14.67	6.25
p-*Tolyl Thiobarbituric acid*										
H^+	10.96	10.93	10.69	2.32	2.16	2.08				
Cu^{2+}	9.38	8.45	7.69	7.12	6.60	6.22	32.15	16.42	67.23	23.98
Zn^{2+}	8.21	7.41	6.72	6.28	5.82	5.45	27.35	14.58	56.18	21.48
Co^{2+}	7.42	6.78	6.22	5.90	5.58	5.22	22.80	12.86	44.11	16.90
Fe^{2+}	7.02	6.45	5.97	5.35	5.02	4.68	19.74	11.40	35.52	14.67
Ni^{2+}	6.75	6.21	5.80	5.10	4.73	4.49	18.24	10.04	31.71	11.51
Mn^{2+}	6.12	5.62	5.30	4.55	4.26	4.13	14.50	7.75	22.10	6.15
o-*Tolyl Thiobarbituric acid*										
H^+	10.71	10.60	10.43	2.19	2.02	1.92				
Cu^{2+}	8.75	7.85	7.12	6.49	6.07	5.64	27.05	14.76	53.19	20.95
Zn^{2+}	7.75	6.96	6.40	5.82	5.36	4.94	22.30	13.24	41.97	19.17
Co^{2+}	7.05	6.35	5.85	5.53	5.15	4.82	18.85	11.99	33.19	16.01
Fe^{2+}	6.70	6.02	5.60	5.08	4.59	4.30	17.22	10.57	29.21	13.94
Ni^{2+}	6.46	5.87	5.42	4.69	4.39	4.10	16.37	9.46	27.07	11.15
Mn^{2+}	5.80	5.35	5.00	4.28	3.99	3.78	11.52	7.44	13.51	6.31

acids with transition metal ions in solution appears to be an enthalpy driven process.

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