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THERMODYNAMICS OF THE INTERACTION OF SOME BIVALENT METAL IONS WITH *N*-ARYLTHIOVIOLURIC ACIDS

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ABSTRACT

Thermodynamic protonation constants of *N*-phenylthiovioluric acid [PTVA], *N*-*p*-tolylthiovioluric acid [*p*-to·TVA], *N*-*o*-tolylthiovioluric acid [*o*-to·TVA] and *N*-*m*-tolylthiovioluric acid [*m*-to·TVA] and thermodynamic formation constants of the chelates of Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+} and Mn^{2+} with these four closely related *N*-arylthiovioluric acids have been determined at three different temperatures in 80% v/v water–dioxane solvent. The stabilities of complexes follow the order of basicities of ligands and also the electron affinities of bivalent metal ions as measured by their overall ionisation potential. Other factors affecting complex stability of the metal ions were discussed. The stepwise complexation is found to be predominantly enthalpy driven processes.

INTRODUCTION

Thiovioluric acids are prominent analytical reagents [1–4]. The importance of these compounds is due partly to their ability to form complexes with a great number of metal ions under different conditions of temperature and acidity. The stabilities of thiovioluric acid and some of its derivatives with various metal ions have been studied by various workers [5–7], but so far *N*-arylthiovioluric acids have not been explored. We present here the results of the potentiometric determination of the formation constants of some bivalent transition metal associates with four closely related *N*-arylthiovioluric acids in an 80% v/v water–dioxane medium at 18, 31 and 42°C.

EXPERIMENTAL

N-Arylthiovioluric acids were obtained by the action of HNO_2 on the corresponding arylthiobarbituric acids which have been synthesised by the method reported

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previously [8]. All the arylthiovioluric acids were used after further purification. The solutions of metal ions were prepared using A.R. grade B.D.H. samples of metal nitrate or sulphate and were standardised by the conventional gravimetric procedures.

Carbonate-free sodium hydroxide was used as the titrant and the titrating solution was made up of $HClO_4$ (0.005 M), ligand (0.01 M) and metal ion (0.001 M). The medium was dioxane–water (1:4 v/v) in which redistilled B.D.H. quality dioxane and double distilled water were used. Titrations were carried out at constant temperature and monitored by a precalibrated Expanded Scale pH-meter (Elico 821, India) equipped with a glass electrode and a saturated calomel electrode. The procedure and computation are essentially based on the method of Irving and Rossotti [9]. The metal–ligand stability constants determined by mid-point slope method, interpolation at half $\bar{n}$ values or interpolation at various $\bar{n}$ values perfectly tally with each other.

Titrations were carried out in triplicate and a ratio of 10:1 of the ligand to metal ion concentration was invariably maintained in order to satisfy the highest possible coordination number of the metal ion under investigation.

RESULTS AND DISCUSSION

In all metal–ligand titrations except in the case of Mn(II), the $\bar{n}$ values steadily increase with pH from < 0.2 to > 1.5 to $\leqslant 2.2$ before precipitation occurs, indicating the formation of 1:2 metal–ligand complexes as the highest complexes in these systems. In the case of Mn(II), all the ligands form 1:1 metal–ligand complexes only. There was no evidence of polynuclear complexes, or influence of Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}, Na^+ on the values of pK_a, K_1 and K_2 under the experimental conditions employed here. The stepwise protonation constants of acids and the stepwise formation constants of the corresponding metal–ligand complexes are given as logarithmic values in Tables 1 and 2. Since activity coefficient corrections have been applied on the basis of the Davies equation [10], pK_a and log K values given here are the thermodynamic constants. Formation constants, determined as above, were reproducible to 0.05 log unit or less in replicate experiments, while variation in the initial concentration of metal and chelating agent gave results with a variation of ± 0.10 log units or less.

Since the reactions leading to the formation of proton–ligand and metal–ligand complexes are similar, the constants pK_a and $\log K_1$ (or $\log K_1 K_2$) should be related linearly, if the factors affecting the bonding of proton and metal ions to the ligand are alike. This is found to be true in the present study. The plots of pK_a vs. $\log K_1$ (or $\log K_1 K_2$) are seen to be straight lines with slopes close to unity indicating that the general relation [11] $\log K = m\,pK_a + C$ is observed.

It is evident from a comparison of Tables 1 and 2 that the introduction of a methyl group into the *ortho, para* and *meta* positions of the *N*-phenyl ring of the PTVA molecule has a parallel effect on the proton–ligand and metal–ligand stability

TABLE I

Thermodynamic stability constants of complexes of *N*-arylthiovioluric acids at different temperatures, and other thermodynamic functions at 31°C

Cation	$\log K_1$			$\log K_2$			Thermodynamic functions at 31°C			
	18°C	31°C	42°C	18°C	31°C	42°C	$-\Delta H_1^0$ (kcal mole^{-1})	$-\Delta H_2^0$ (kcal mole^{-1})	$-\Delta S_1$ (cal mole^{-1} deg^{-1})	$-\Delta S_2$ (cal mole^{-1} deg^{-1})
N-Phenylthiovioluric acid										
H^+	11.19	10.88	10.74	5.22	4.95	4.82				
Co^{2+}	9.39	8.25	7.72	7.12	6.60	6.40	33.97	14.13	74.14	16.42
Cu^{2+}	9.08	8.00	7.53	6.80	6.25	5.99	30.92	12.99	65.23	14.24
Zn^{2+}	7.90	7.05	6.65	6.45	5.84	5.63	23.25	12.31	44.34	13.88
Fe^{2+}	7.74	6.90	6.55	6.04	5.58	5.40	20.06	11.22	34.54	11.48
Ni^{2+}	7.55	6.80	6.42	5.86	5.45	5.30	18.24	10.16	29.02	8.58
Mn^{2+}	6.38	5.90	5.65				12.13		13.02	
N-p-Tolylthiovioluric acid										
H^+	11.33	11.03	10.88	5.55	5.27	5.14				
Co^{2+}	9.53	8.40	7.84	7.55	7.03	6.77	34.33	14.68	74.63	16.25
Cu^{2+}	9.18	8.05	7.50	7.02	6.45	6.17	31.92	13.68	68.28	15.59
Zn^{2+}	8.10	7.30	6.90	6.55	6.05	5.80	23.72	12.63	44.70	13.98
Fe^{2+}	7.84	7.05	6.70	6.47	5.88	5.65	22.80	12.32	42.86	13.68
Ni^{2+}	7.78	6.95	6.62	6.05	5.66	5.46	19.24	11.40	31.62	11.72
Mn^{2+}	6.58	6.08	5.82				14.18		18.94	

TABLE 2

Thermodynamic stability constants of complexes of *N*-arylthiovioluric acid at different temperatures, and other thermodynamic functions at 31°C

Cation	log K_1			log K_2			Thermodynamic functions at 31°C			
	18°C	31°C	42°C	18°C	31°C	42°C	ΔH_1^0 (kcal mole^{-1})	$-\Delta H_2^0$ (kcal mole^{-1})	$-\Delta S_1^0$ (cal mole^{-1} deg^{-1})	ΔS_2^0 (cal mole^{-1} deg^{-1})
N-o-Tolylthiovioluric acid										
H^+	10.98	10.70	10.57	4.85	4.62	4.50				
Co^{2+}	9.26	8.10	7.54	7.10	6.55	6.30	32.46	12.67	69.83	11.80
Cu^{2+}	8.92	7.80	7.32	6.52	6.08	5.85	30.78	12.00	65.69	11.77
Zn^{2+}	7.64	6.80	6.37	6.10	5.62	5.42	22.57	10.94	43.25	10.36
Fe^{2+}	7.52	6.70	6.30	5.75	5.30	5.10	20.97	10.26	38.45	9.60
Ni^{2+}	7.29	6.50	6.20	5.55	5.12	4.93	18.78	9.22	32.13	6.97
Mn^{2+}	6.32	5.88	5.60				12.63		14.73	
N-m-Tolylthiovioluric acid										
H^+	11.14	10.82	10.72	5.16	4.90	4.78				
Co^{2+}	9.45	8.62	7.73	7.18	6.67	6.45	33.02	13.13	69.30	12.79
Cu^{2+}	9.05	7.90	7.35	6.77	6.26	6.05	31.23	12.40	66.74	12.26
Zn^{2+}	7.79	7.18	6.88	6.25	5.78	5.58	23.25	11.58	43.75	11.74
Fe^{2+}	7.70	6.75	6.35	5.88	5.48	5.25	22.34	10.62	42.73	9.96
Ni^{2+}	7.50	6.60	6.25	5.74	5.32	5.16	19.52	9.52	34.07	7.07
Mn^{2+}	6.35	5.92	5.72				13.22		16.52	

constants; for example, the pK_a order is *p*-to · TVA > PTVA > *m*-to · TVA > *o*-to · TVA 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 can hardly be transmitted to the coordination centre located far from it. But there does exist an unmistakable gradation, albeit small, as shown above. The substituent effect in interactions of this and phenyl groups then operates through the *N*-heterobenzenoid ring and affects 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 in spite of a chelate ring, most probably non-coplanar with the thioviolurate ring, being produced.

The order of the stability of metal complexes with all the ligands is

$$\mathrm{Co}^{2+} > \mathrm{Cu}^{2+} > \mathrm{Zn}^{2+} > \mathrm{Fe}^{2+} > \mathrm{Ni}^{2+} > \mathrm{Mn}^{2+}$$

Except for the Co(II) complex, this sequence is in agreement with that found by Irving and William. The abnormal high stability of Co(II) complexes indicates that in solution the Co(II) is transferred to the Co(III) complex. The study of Moratal and Faus [12] on the Co(II) complexes of thiovioluric acids has conclusively proved this point. The greater stability of Cu(II) complexes is produced by the well known Jahn-Teller effect. The relatively low values of Ni^{2+} can be attributed to steric hindrance preventing the formation of a square planar structure [13].

The ratio of successive stability constants, $\log(K_1/K_2)$, is found to be positive in all systems. Furthermore, it is observed that the values of log K_2 are lower than log K_1, by nearly 1.5–2.0 units. This implies that in these systems not only the statistical effect, which gives $\log K_1 - \log K_2 = 0.60$ units, is to be considered but the electrostatic effect and the steric hindrance to the addition of the second chelate group are also significant. In the case of chelating agents containing bulky substituents [14] near the donor atoms, steric hindrance to the addition of the second group causes $\log K_1/K_2$ to be unusually high.

The values of pK_a and log *K* at higher temperatures indicate that the temperature increases the acidity of the ligands and reduces the stabilities of the complexes, but to a smaller degree. Since log *K* values vary linearly with $1/T$, the enthalpy of complexation was determined by the van't Hoff equation

$$\frac{\mathrm{d}\log K}{\mathrm{d}t} = \frac{\Delta H^\circ}{2.303RT^2}$$

The free energy change ΔG°, and ΔS° were calculated from the relationships

$$-\Delta G^\circ = 2.303\ RT\log K$$

and

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T$$

Considering that thioviolurate ions and bivalent metal cations behave as soft donor and soft acceptor, respectively, the complexation reaction must be exothermic. 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. Being soft acceptors, thioviolurates are expected to be weakly solvated and the extent of charge neutralisation on associating with metal ions in solution 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 *N*-arylthiovioluric acids with these bivalent metal ions in solution appears to be an enthalpy driven process. In addition, there is stronger dependence of log K on I_{O_2}. So it may be concluded that the metal-ligands have more of a covalent character.

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