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Note

BINARY AND TERNARY COMPLEXES OF INTEREST TO ENVIRONMENTAL SYSTEMS. VIII. EFFECT OF TEMPERATURE ON THE COMPLEX EQUILIBRIA INVOLVING Cu(II), HETEROCYCLIC HYDROXAMIC ACIDS, AND 2,2'-BIPYRIDYL

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Hydroxamic acids have been attracting increasing attention in recent years owing to their importance as analytical reagents [1—7], anti-tumour drugs [8] and deodorants [9]. In order to understand the mechanism of action of the hydroxamic acids and to make a rational application of these compounds in analytical, medicinal and environmental chemistry, a programme of studies on the formation and stabilities of their binary and ternary complexes has been undertaken. In the present study, which is part of this continuing programme [7,10—14], we report the interaction of Cu(II) or Ni(II) with 2,2'-bipyridyl (bipy) and one of the following: *N*-phenyl-2-furohydroxamic acid (PFHA), *N*-*m*-tolyl-2-furohydroxamic acid (mTFHA), *N*-*p*-tolyl-2-furohydroxamic acid (pTFHA), *N*-phenyl-2-thenohydroxamic acid (PTHA), *N*-*m*-tolyl-2-thenohydroxamic acid (mTTHA) and *N*-*p*-tolyl-2-thenohydroxamic acid (pTTHA). Copper(II) and Ni(II) have been chosen for the present study because they are essential for many of the biological systems [15] while bipy has been chosen because of its importance as an analytical reagent [16] and a drug [17]. PFHA [18], PTHA [19] and pTTHA [19] have already been used as sensitive and selective analytical reagents.

EXPERIMENTAL

The hydroxamic acids were prepared and purified by the general method of Tandon and Bhattacharyya [19]. Dioxane (Merck) was purified by Frieser's method [20]. Standard metal ion solutions were prepared by the usual methods and de-ionized water was used throughout.

Potentiometric titrations were performed with thermostated 50 ml solutions in 50% v/v dioxane—water mixtures containing 1.0×10^{-3} M or 0.5×10^{-3} M solutions of (a) hydroxamic acid, (b) hydroxamic acid + metal ion, (c) bipy (d) bipy + metal ion, or (e) hydroxamic acid + metal ion + bipy. In addition, titrations were performed on binary systems containing metal : ligand ratios of 1 : 10 to study the binary complexes. The solutions were purged with nitrogen gas which had been passed through a train of troughs containing pyrogallic acid, concentrated KOH solution and a 50% v/v dioxane—water mixture. The rest of the titration procedure and method of calculation of the thermodynamic protonation constants were essentially as detailed by Goldberg [21]. The thermodynamic first and second formation constant, K_1 and K_2, respectively defined as

$$K_1 = \frac{[\mathrm{MA}^+]}{[\mathrm{M}^{2+}][\mathrm{A}^-]}\,\frac{\gamma_{\mathrm{MA}^+}}{\gamma_{\mathrm{M}^{2+}}\gamma_{\mathrm{A}^-}}$$

$$K_2 = \frac{[\mathrm{MA}_2]}{[\mathrm{MA}^+][\mathrm{A}^-]}\,\frac{\gamma_{\mathrm{MA}_2}}{\gamma_{\mathrm{MA}^+}\gamma_{\mathrm{A}^-}}$$

and the thermodynamic formation constants of ternary complexes, K_m defined as

$$K_m = \frac{[\mathrm{MBA}^+]}{[\mathrm{MB}^+][\mathrm{A}^-]}\,\frac{\gamma_{\mathrm{MBA}^+}}{\gamma_{\mathrm{MB}^+}\gamma_{\mathrm{A}^-}}$$

where M represents the metal ion and A and B represent the hydroxamic acid and bipy, respectively, were computed with the help of a computer program CECADS, written in Fortran IV and run on a DEC-10 computer. All titrations were done with at least two metal concentrations, differing from each other by factors of 5—10. The dioxane—water mixture was used because the hydroxamic acids employed in the present study are all sparingly soluble in water while their complexes are insoluble in water.

RESULTS AND DISCUSSION

Stoichiometry of the complexes

In the binary complexes involving hydroxamic acids, the n value at 25°C, as well as 35°C, steadily increased with pH from <0.2 to $>1.5 \leqslant 2$ before precipitation occurred, indicating the formation of 1 : 2 metal—ligand complexes as the highest complexes in these systems. In the complexes involving Ni(II) and bipy, the $\bar{n}$ value increased beyond 2 but precipitation occurred soon afterwards leaving insufficient data for the calculation of K_3 values.

In the ternary systems, stepwise formation of mixed ligand complexes was observed at both the temperatures when titrations were done in the sequence described in the experimental section. The 1 : 1 metal—bipy complexes were formed at pH < 4 which subsequently added the hydroxamic acid molecules at higher pH values to form 1 : 1 : 1 ternary complexes. The analysis of the titration curves was carried out in the same fashion as detailed elsewhere for ternary complexes involving nicotino- and isonicotinohydroxamic acids [23].

Thermodynamic constants

All the values are collected in Tables 1—4.

The basicity of PFHA or PTHA and their derivatives is higher than the overall basicity of bipy (Tables 1—2) but the overall stabilities of the

TABLE 1

Thermodynamic protonation constants of hydroxamic acids in 50% v/v dioxane—water

Ligand	$\log K_{\mathrm{H}_1}$		ΔH^0 (kcal mole^{-1})
	25°C	35°C	
PFHA	10.59 ± 0.01	10.48 ± 0.01	4.63
mTFHA	10.64 ± 0.01	10.53 ± 0.02	4.63
pTFHA	10.68 ± 0.01	10.56 ± 0.01	5.47
PTHA	10.86 ± 0.01	10.73 ± 0.02	5.47
mTTHA	10.90 ± 0.01	10.78 ± 0.01	5.05
pTTHA	10.95 ± 0.02	10.83 ± 0.02	5.05

TABLE 2

Thermodynamic proton—ligand and metal—ligand complexes involving 2,2′-bipyridyl in 50% v/v dioxane—water

Metal	$\log K_1$		ΔH_1^0 (kcal mole^{-1})	$\log K_2$		ΔH_2^0 (kcal mole^{-1})
	25°C	35°C		25°C	35°C	
H^+	5.75	5.60	6.30	2.65	2.58	2.92
Cu(II)	9.26	9.12	5.88	7.72	7.61	4.62
Ni(II)	7.84	7.70	5.88	7.47	7.33	5.88

TABLE 3

Thermodynamic stability constants of binary and ternary complexes of Cu(II) in 50% v/v dioxane—water

Ligand	$\log K_1$		ΔH_1^0	$\log K_2$		ΔH_2^0	$\log K_m$		ΔH_m^0
	25°C	35°C		25°C	35°C		25°C	35°C	
PFHA	8.90	8.80	4.21	7.40	7.35	2.1	9.06	8.95	4.63
mTFHA	8.94	8.83	4.63	7.41	7.34	1.47	9.10	8.99	4.63
pTFHA	8.97	8.89	3.36	7.43	7.35	3.36	9.17	9.08	3.79
PTHA	9.08	8.97	4.63	7.52	7.40	5.05	9.27	9.17	4.21
mTTHA	9.11	9.01	4.21	7.54	7.42	5.05	9.29	9.20	3.79
pTTHA	9.15	9.05	4.21	7.56	7.43	5.47	9.32	9.21	4.63

TABLE 4

Thermodynamic stability constants of binary and ternary complexes of Ni(II) in 50% v/v dioxane—water

Ligand	$\log K_1$		ΔH_1^0	$\log K_2$		ΔH_2^0	$\log K_m$		ΔH_m^0
	25°C	35°C		25°C	35°C		25°C	35°C	
PFHA	5.92	5.86	2.52	5.01	4.97	1.68	6.01	5.90	4.68
mTFHA	5.95	5.89	2.52	5.03	4.97	2.52	6.08	5.97	4.68
pTFHA	5.99	5.91	3.36	5.05	4.98	2.94	6.11	6.01	4.20
PTHA	6.10	6.01	3.78	5.12	5.02	4.20	6.24	6.15	3.78
mTTHA	6.12	6.02	4.20	5.14	5.05	3.78	6.27	6.17	4.20
pTTHA	6.15	6.04	4.62	5.16	5.06	4.20	6.30	6.18	5.04

binary metal—ligand complexes involving bipy (Table 2) are higher than the corresponding values involving hydroxamic acids (Tables 3—4). This is probably due to the preference of the 3*d* metal ions for nitrogen donors compared with oxygen donors [24].

In all cases, log K_m values are higher than log K_1 values for the metal—hydroxamic acid systems. This indicates that addition of the hydroxamic anion to the 1 : 1 metal—bipy complex gives a more thermodynamically stable system than the addition of the former to the unchelated metal ion. This observation is unusual because more coordination positions are available to the hydroxamate ion during formation of the 1 : 1 complex than in the latter case. A possible reason may be the bonding between the $p\pi$ orbitals of bipy and the $d\pi$ orbitals of the 3*d* metal ions. The experiments reported elsewhere with Cu(II)—bipy—pyrocatechol and Cu(II)—ethylenediamine—pyrocatechol [25], and Cu(II)—bipy—oxalic acid and Cu(II)—ethylenediamine—oxalic acid [26] systems have also revealed that the mixed complexes involving bipy have unusually high stability compared with similar complexes involving ethylenediamine. Like bipy, ethylenediamine has nitrogen atoms as donor sites and is a neutral ligand, but unlike bipy, it has no $p\pi$ orbitals available for "back-donation" to the metal ion.

The "hard and soft rule" of Pearson [27] also provides some insight into present experimental observations. This rule, which deals with the Lewis-type acids and bases, states that hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases. According to Pearson, Cu(II) and Ni(II) are neither hard nor soft but are border line; the same is true for the pyridyl group. Since bonds are formed and back-donation occurs from metal ions to bipy, the *d* electron content of metal ions decreases, i.e. they become more hard. Hence, through the combination of border-line bipy with the border-line metal ion, a hard species is created which is more favoured to combine with oxygen donors than with nitrogen donors (the hardness increases in the order: $CH_3^- < NH_2^- < OH^- < F^-$).

At both the temperatures studied, the protonation constants of tolyl derivatives of PFHA as well as TFHA are higher than the corresponding constants of the parent ligands due, probably, to the inductive electron-donating tendencies of the methyl substituents.

The values of the standard enthalpy change, ΔH^0, were calculated using van't Hoff's equation [28] for temperatures T_1 (298 K) and T_2 (308 K)

$$\frac{\log K_2}{\log K_1} = \frac{\Delta H^\circ (T_2 - T_1)}{4.567 T_1 T_2}$$

In all cases (Tables 1—4), ΔH^0 is positive and values of the formation constant for proton-ligand as well as binary and ternary metal-ligand complexes are lower at higher temperatures. The formation reactions are thus endothermic in nature and the thermodynamic stabilities are adversely affected by temperature.

The complexes involving hydroxamic acids (Tables 3—4) follow the order of basicity of corresponding ligands indicating that the temperature and the substituents affect the proton affinity of the ligands in the same way as their metal ion affinity.

The stabilities of the Cu(II) complexes are greater than those of the corresponding complexes of Ni(II) by several orders of magnitude. Our unpublished studies on the electron spin resonance spectra of ternary complexes [29] have indicated the presence of Jahn—Teller distortion in the complexes involving Cu(II), as a result of which the octahedral symmetry in the Cu(II) ion is distorted and the complexes get extra stabilisation. The Cu(II) ion with its d^9 configuration provides one of the best opportunities for observation of the Jahn—Teller effect to an appreciable extent.

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