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Note

HETEROCYCLIC HYDROXAMIC ACIDS. V. THERMODYNAMICS OF THE INTERACTION OF SOME BIVALENT METAL IONS WITH *N*-PHENYL-2-FUROHYDROXAMIC ACID AND ITS ANALOGUES

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Hydroxamic acids are prominent analytical reagents [1—3] and drugs [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. In continuation of our studies [2,3,5,6] on the correlation of temperature, basicity and metal complex stability of heterocyclic hydroxamic acids with their effectiveness as analytical and medicinal reagents, we present here potentiometric studies on the interaction of *N*-phenyl-2-furohydroxamic acid (PFHA), *N*-*o*-tolyl-2-furohydroxamic acid (*o*-TFHA) and *N*-*m*-tolyl-2-furohydroxamic acid (*m*-TFHA) with several metal ions at two temperatures. PFHA and some of its analogues have been employed successfully as sensitive and selective analytical reagents [1—3].

EXPERIMENTAL

Hydroxamic acids were prepared and purified by methods reported previously [7]. pH titrations were performed with thermostated 50 ml solutions of hydroxamic acids in 50% v/v dioxane—water mixtures containing 1×10^{-3} M $HClO_4$ with and without metal ions. Nitrogen gas, purified from pyrogallic acid and concentrated KOH solutions and pre-saturated with a 50% v/v dioxane—water mixture, was bubbled through the titre solution. The rest of the titration procedure is essentially an extension of the Bjerrum—Calvin pH titration method as detailed by Goldberg [8]. The thermodynamic ionisation and first and second stability constants, K_a, K_1 and K_2, respectively, defined as

$$K_a = \frac{[HA]}{[H^+][A^-]} \frac{\gamma_{HA}}{\gamma_{H^+}\gamma_{L^-}}$$

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

and

$$K_2 = \frac{[MA_2]}{[MA^+][A^-]} \frac{\gamma_{MA_2}}{\gamma_{MA^+}\gamma_{A^-}}$$

were computed by a computer program CECADS, written in Fortran-IV [9] and run on a DEC-10 computer. The method of calculation is based on that of Irving and Rossotti [10] but takes into account all possible equilibria. The correction factors for conversion of pH meter readings to hydrogen ion activities in a 50% v/v dioxane—water system were taken from the data of Van Uitert and Hass [11], and activity coefficients were computed from tables of Harned and Owen [12].

Titrations were performed repeatedly until two sets of values differing within ±0.001 pH units were obtained. All titrations were done with at least two different metal concentrations, differing by factors of 5—10.

RESULTS AND DISCUSSION

The results are summarised in Tables 1—4. In all metal—ligand titrations, the $\bar{n}$ value steadily increased with pH from <0.2 to $>1.5 \leqslant 2$ before precipitations occurred, indicating the formation of 1 : 2 metal—ligand complexes as the highest complexes in these systems. There was no evidence of polynuclear complexes, protonated complexes or influence of Cl^-, ClO_4^-, NO_3^-, Na^+, K^+ on values of pK_a, K_1 and K_2. Some typical formation curves are shown in Fig. 1.

It has been shown [13] that the pH for 50% precipitation or 50% extraction of metal complexes, for a constant excess of the ligand, is a measure of their relative stability, and vice versa. In the present study it is observed that the stability constants of the complexes of each of the ligands follow the order $UO_2^{2+} > Pd^{2+} > Cu^{2+} >> Ni^{2+} > Co^{2+} > Mn^{2+} < Zn^{2+}$.

The stability sequence from Pd^{2+} to Zn^{2+} follows the Irving—Williams order [13] while the order $UO_2^{2+} > Cu^{2+}$ is in accordance with the greater affinity of UO_2^{2+} for —O, —O, donors than Cu^{2+} [14].

The stabilities of copper complexes are considerably higher then those of the other metals of the 3-*d* series, and values for Zn^{2+} are greater than Ni^{2+}. The relatively low values for Ni^{2+} can be attributed to steric hindrance pre-

TABLE 1

Thermodynamic ionisation constants in 50% v/v dioxane—water

Hydroxamic acid	pK_a		$\Delta H°$ (kcal mole^{-1})
	25°C	35°C	
N-Phenyl-2-furo-	10.59	10.48	4.63
N-*o*-Tolyl-2-furo-	10.73	10.61	5.04
N-*m*-Tolyl-2-furo-	10.64	10.52	4.21

TABLE 2

Thermodynamic metal—ligand stability constants of complexes of N-phenyl-2-furohydroxamic acid in 50% v/v dioxane—water

Metal ion	log K_1		log K_2		log K_1/K_2		ΔH° (kcal mole^{-1})	
	25°C ± 0.1	35°C ± 0.1	25°C ± 0.1	35°C ± 0.1	25°C ± 0.1	35°C ± 0.1	log K_1	log K_2
UO^{2+}	9.68	9.58	8.37	8.31	1.31	1.27	4.2	2.5
Pd^{2+}	9.00	8.92	7.64	7.55	1.38	1.37	3.4	3.8
Cu^{2+}	8.90	8.81	7.40	7.35	1.49	1.46	3.8	2.1
Zn^{2+}	6.53	6.45	5.71	5.65	0.83	0.80	3.4	2.5
Ni^{2+}	5.93	5.85	5.01	4.96	0.92	0.89	3.4	2.1
Co^{2+}	5.70	5.62	4.83	4.78	0.87	0.84	3.4	2.1
Mn^{2+}	5.10	5.04	4.37	4.34	0.73	0.70	2.5	1.3

TABLE 3

Thermodynamic metal—ligand stability constants of complexes of N-*o*-tolyl-2-furohydroxamic acid in 50% v/v dioxane—water

Metal ion	log K_1		log K_2		*log* K_1/K_2		ΔH° (kcal mole^{-1})	
	25°C ± 0.1	35°C ± 0.1	25°C ± 0.1	35°C ± 0.1	25°C ± 0.1	35°C ± 0.1	log K_1	log k_2
UO^{2+}	9.22	9.11	8.05	7.98	1.17	1.13	4.6	2.9
Pd^{2+}	8.65	8.57	7.10	7.00	1.55	1.57	3.4	4.2
Cu^{2+}	8.53	8.46	6.72	6.64	1.81	1.82	2.9	3.4
Zn^{2+}	6.25	6.18	5.23	5.17	1.02	1.01	2.9	2.5
Ni^{2+}	5.65	5.57	4.57	4.49	1.08	1.08	3.4	3.4
Co^{2+}	5.51	5.47	4.50	4.38	1.01	1.09	1.7	5.0
Mn^{2+}	4.90	4.82	4.01	3.92	0.89	0.90	3.4	3.8

TABLE 4

Thermodynamic metal—ligand stability constants of complexes of N-*m*-tolyl-2-furohydroxamic acid in 50% v/v dioxane—water

Metal ion	log K_1		log K_2		log K_1/K_2		ΔH° (kcal mole^{-1})	
	25°C ± 0.1	35°C ± 0.1	25°C ± 0.1	35°C ± 0.1	25°C ± 0.1	35°C ± 0.1	log K_1	log K_2
UO^{2+}	9.70	9.59	8.40	8.33	1.30	1.26	4.6	2.9
Pd^{2+}	9.05	8.95	7.66	7.57	1.39	1.38	4.2	3.8
Cu^{2+}	8.93	8.85	7.43	7.38	1.50	1.57	3.4	2.1
Zn^{2+}	6.54	6.46	5.73	5.66	0.81	0.80	3.4	2.9
Ni^{2+}	5.95	5.88	5.03	4.97	0.92	0.91	2.9	2.5
Co^{2+}	5.73	5.64	4.84	4.79	0.89	0.85	3.8	2.1
Mn^{2+}	5.12	5.05	4.39	4.35	0.73	0.70	2.9	1.7

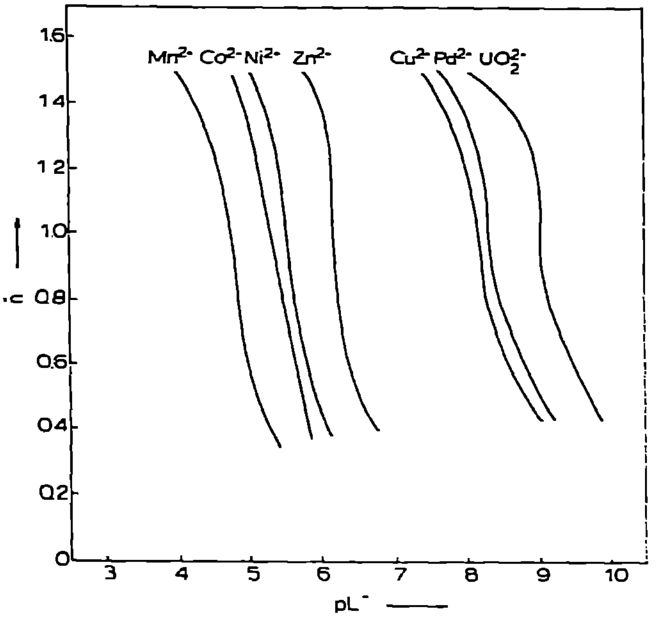

Fig. 1. Formation curves of complexes of *N*-phenyl-2-furohydroxamic acid.

venting the formation of a square planar structure [15], while the observation $Cu^{2+} >> Ni^{2+}$ can be explained by the Jahn—Teller effect, by virtue of which Cu^{2+} complexes will gain extra stabilisation. Plots of stability constants of Zn^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} with their overall ionisation potentials are linear (Fig. 2), a relationship observed by many authors [16].

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 0.7—1.5 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 is also significant.

The introduction of methyl groups in *o*- and *m*-TFHA increases their basicity relative to PFHA (Table 1), presumably due to a positive inductive

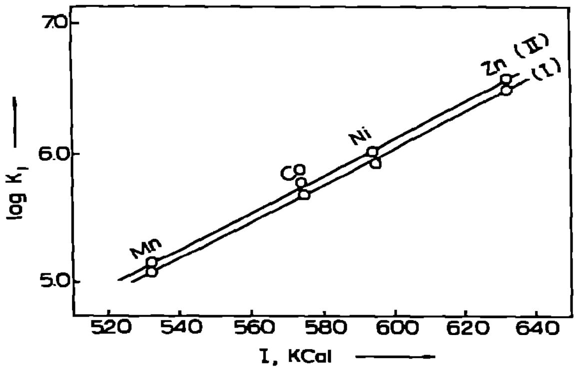

Fig. 2. Complexes involving (I) *N*-phenyl-2-furohydroxamic acid and (II) *N*-*m*-tolyl-2-furohydroxamic acid.

effect. With the increase in proton affinity in *o*-TFHA and *m*-TFHA, their metal ion affinity also increases, as reflected by the stability constants. It is seen that although the basicity of *o*-TFHA > *m*-TFHA, the stabilities of complexes of *o*-TFHA < *m*-TFHA. The steric hindrance due to the *ortho*-methyl group during metal—*o*-TFHA interaction is the possible reason for this observation.

The values at 35°C indicate that temperature increases the acidity of the ligands and reduces the stabilities of the complexes, but to a small degree. The values of standard enthalpy change, ΔH^0, calculated using van't Hoff's equation [17] at two temperatures, T_1(198 K) and T_2(309 K)

$$\Delta H^0 = \frac{4.576(\log K_1 - \log K_2)}{\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]}$$

are positive for the proton—ligand as well as metal—ligand equilibria studied, but fail to reveal any other trend.

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