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Note

A thermodynamic study on the complexes of some divalent metal ions with *ortho* substituted N-phenylbenzohydroxamic acids

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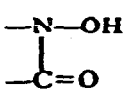
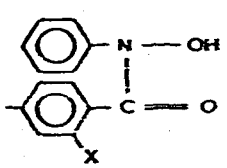
Hydroxamic acids are bidentate ligands, having the functional grouping (I):



(I)

They react with metal ions and form the complexes of immense analytical importance. A study has been initiated on the thermodynamic interaction of such metal ions with hydroxamic acids. For such systems the formation constant data are available at 25°C only[1]. In the present paper the work has been extended on the thermodynamic metal–ligand stability constants to 35°C. The enthalpy changes (ΔH°) and entropy changes (ΔS°) associated with the formation of complexes of several N-phenyl-*o*-substituted hydroxamic acids (II) with Cu, Zn, Ni and Mn are reported.



EXPERIMENTAL

Chemicals

All chemicals used were of AnalaR and G.R. grades of B.D.H. and E. Merck, respectively.

Reagent and apparatus

Carbonate-free potassium hydroxide was prepared by the method of Vogel[2]. The metal perchlorates were prepared by treating excess of carbonates with perchloric

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acid and the concentrations of the metal ions in solutions were determined volumetrically[3]. A 1,4-dioxane was purified by the procedure of Weissberger[4].

A Beckman digital pH meter equipped with Beckman glass and calomel electrode was used for pH metric measurements.

Procedure

The details of the procedure and calculations for the metal–ligand stability constants were described elsewhere[1,5,6].

RESULTS AND DISCUSSION

The thermodynamic metal–ligand stability constants for divalent metal ions (Cu^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+}) with substituted N-phenylbenzohydroxamic acids are recorded in Table 1. The mole ratio of metal to hydroxamic was kept 1:10 in

TABLE 1

THERMODYNAMIC METAL–LIGAND STABILITY CONSTANTS OF *ortho*-SUBSTITUTED N-PHENYLBENZOHYDROXAMIC ACIDS AT 25 AND 35°C IN 50% AQUEOUS DIOXANE MEDIA

The values at 35°C are given in parenthesis and the others are at 25°C.

Metal ions	*Constants*	*Substituent, X*						
		CH_3	CH_3O	*F*	*Cl*	*Br*	*I*	NO_2
Cu^{2+}	$\log K_1$	10.45	10.55	10.20	10.14	10.11	10.15	9.70
		(10.25)	(10.35)	(10.03)	(9.96)	(9.90)	(9.96)	(9.45)
	$\log K_2$	8.75	8.90	8.20	8.15	8.12	8.16	7.70
		(8.56)	(8.68)	(8.08)	(8.04)	(7.97)	(8.12)	(7.49)
	$\log K_1K_2$	26.20	26.55	25.11	24.96	24.88	24.99	23.75
		(18.81)	(19.03)	(18.11)	(18.00)	(17.87)	(18.08)	(16.44)
Zn^{2+}	$\log K_1$	8.04	8.84	7.61	7.67	7.65	7.58	7.22
		(7.86)	(8.63)	(7.40)	(7.52)	(7.49)	(7.40)	(7.12)
	$\log K_2$	6.40	6.82	5.80	6.07	6.03	5.96	5.64
		(6.21)	(6.65)	(5.69)	(5.92)	(5.87)	(5.64)	(5.44)
	$\log K_1K_2$	14.44	15.66	13.41	13.74	13.68	13.54	12.86
		(14.07)	(15.28)	(13.09)	(13.44)	(13.36)	(13.04)	(12.56)
Ni^{2+}	$\log K_1$	7.99	8.01	7.55	7.30	7.35	7.38	7.15
		(7.82)	(7.77)	(7.36)	(7.23)	(7.21)	(7.23)	(7.07)
	$\log K_2$	6.00	5.72	5.60	5.58	5.45	5.43	5.06
		(5.86)	(5.68)	(5.54)	(5.45)	(5.33)	(5.30)	(5.04)
	$\log K_1K_2$	13.99	13.73	13.15	12.88	12.78	12.81	12.21
		(13.68)	(13.45)	(12.90)	(12.68)	(12.54)	(12.53)	(12.11)
Mn^{2+}	$\log K_1$	6.61	6.98	6.30	6.22	6.25	6.19	5.90
		(6.46)	(6.80)	(6.10)	(6.04)	(6.07)	(6.02)	(5.74)
	$\log K_2$	4.92	5.85	5.08	5.11	4.94	4.84	4.54
		(4.77)	(5.67)	(4.88)	(4.93)	(4.76)	(4.68)	(4.38)
	$\log K_1K_2$	11.53	12.83	11.38	11.33	11.19	11.03	10.44
		(11.23)	(12.47)	(10.98)	(10.97)	(10.83)	(10.70)	(10.12)

order to fulfil the maximum coordination number of metal ion. The maximum $\bar{n}$ value for all the complexes was 2, indicating the formation of 1:1 and 1:2 complexes.

For the calculation of the thermodynamic parameters the following relationships were used

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

$$\log K_2/K_2 = \frac{\Delta H^\circ(T_2 - T_1)}{4.576\,T_1\,T_2}$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

The values of free energy of formation (ΔG°) enthalpy changes (ΔH°) and entropy changes (ΔS°) are summarised in Table 2–4.

TABLE 2

FREE ENERGY DATA (in kcal mol^{-1}) OF METAL–HYDROXAMIC ACID COMPLEXES

The values at 35°C are given in parentheses and the others are at 25°C

Metal ions	*Constants*	*ΔG° values Substituent, X*						
		CH_3	*CH_3O*	*F*	*Cl*	*Br*	*I*	*NO_2*
Cu^{2+}	$\log K_1$	14.26 (14.46)	14.40 (14.60)	13.92 (14.15)	13.84 (14.05)	13.80 (13.97)	18.85 (14.05)	13.24 (13.33)
	$\log K_2$	11.94 (12.08)	12.15 (12.25)	11.19 (11.40)	12.12 (11.34)	11.08 (11.25)	11.14 (11.46)	10.51 (10.57)
	$\log K_1K_2$	26.20 (26.54)	26.55 (26.85)	25.11 (25.55)	24.96 (25.39)	24.88 (25.22)	24.99 (25.51)	23.75 (23.92)
Zn^{2+}	$\log K_1$	10.97 (11.09)	12.07 (12.18)	10.39 (10.44)	10.47 (10.61)	10.44 (10.57)	10.35 (10.44)	9.85 (10.05)
	$\log K_2$	8.79 (6.76)	9.31 (9.38)	7.82 (8.03)	8.29 (8.35)	8.23 (8.28)	8.13 (7.96)	7.70 (7.68)
	$\log K_1K_2$	19.71 (19.85)	21.38 (21.56)	18.31 (18.47)	18.76 (18.96)	19.67 (18.85)	18.48 (18.40)	17.55 (17.72)
Ni^{2+}	$\log K_1$	10.91 (11.03)	10.93 (10.96)	10.31 (10.38)	9.96 (10.20)	10.03 (10.17)	10.07 (10.20)	9.78 (9.98)
	$\log K_2$	8.18 (8.27)	7.81 (8.01)	7.64 (7.82)	7.62 (7.69)	7.44 (7.52)	7.41 (7.48)	6.91 (7.11)
	$\log K_1K_2$	19.10 (19.30)	18.74 (18.98)	17.95 (18.20)	17.58 (17.89)	17.44 (17.69)	17.49 (17.68)	16.67 (17.09)
Mn^{2+}	$\log K_1$	9.02 (9.12)	9.53 (9.59)	8.60 (8.61)	8.49 (8.52)	8.53 (8.56)	8.45 (8.49)	8.05 (8.10)
	$\log K_2$	6.94 (6.73)	8.24 (8.00)	7.17 (6.88)	7.21 (6.96)	6.97 (6.72)	6.83 (6.60)	6.41 (6.18)
	$\log K_1K_2$	15.74 (15.85)	17.51 (17.60)	15.53 (15.49)	15.46 (15.48)	15.27 (15.28)	15.06 (15.10)	14.25 (14.28)

TABLE 3

ENTHALPY DATA (in kcal mol^{-1}) OF METAL–HYDROXAMIC ACID COMPLEXES

Metal ions	*Constants*	$-\Delta H^{\circ}$ *values*[1] *Substituent, X*						
		CH_3	CH_3O	F	Cl	Br	I	NO_2
Cu^{2+}	$\log K_1$	8.41	8.41	7.15	7.57	8.83	7.99	10.52
	$\log K_2$	7.99	9.26	5.05	4.63	6.31	1.68	8.83
	$\log K_1K_2$	16.41	17.67	12.20	12.20	15.15	9.68	19.35
Zn^{2+}	$\log K_1$	7.57	8.83	8.83	6.31	7.15	7.57	4.21
	$\log K_2$	7.99	7.15	4.63	6.31	6.73	13.46	8.41
	$\log K_1K_2$	15.57	15.97	13.46	12.62	13.46	21.04	12.62
Ni^{2+}	$\log K_1$	7.15	10.10	7.99	2.94	5.89	6.31	3.37
	$\log K_2$	5.89	1.68	2.52	4.63	5.05	4.47	0.84
	$\log K_1K_2$	13.04	11.78	10.52	8.41	10.10	11.78	4.21
Mn^{2+}	$\log K_1$	6.31	7.57	8.41	7.57	7.57	7.15	6.73
	$\log K_2$	6.31	7.57	8.41	7.57	7.57	6.73	6.73
	$\log K_1K_2$	12.62	15.14	16.83	15.14	15.14	13.88	13.46

TABLE 4

ENTROPY DATA (in cal deg^{-1} mol^{-1}) OF METAL–HYDROXAMIC ACID COMPLEXES

The values at 35°C are given in parentheses and the others are at 25°C

Metal ions	*Constants*	ΔS° *values*[1] *Substituent X*						
		CH_3	CH_3O	F	Cl	Br	I	NO_2
Cu^{2+}	$\log K_1$	19.62	20.09	22.71	21.03	16.67	19.65	9.12
		(19.63)	(20.08)	(22.71)	(21.02)	(16.67)	(19.66)	(9.12)
	$\log K_2$	13.25	9.69	20.59	21.77	16.00	31.63	5.63
		(13.27)	(9.70)	(20.60)	(21.77)	(16.03)	(31.73)	(5.64)
	$\log K_1K_2$	33.17	29.78	43.30	42.80	32.63	51.35	14.76
		(32.86)	(29.78)	(43.31)	(42.79)	(32.67)	(51.35)	(14.83)
Zn^{2+}	$\log K_1$	11.40	10.87	5.23	13.95	7.68	9.32	18.92
		(11.42)	(10.87)	(5.22)	(13.95)	(11.09)	(9.31)	(18.94)
	$\log K_2$	2.52	7.24	11.03	6.64	8.38	−17.88	−2.38
		(3.99)	(7.23)	(11.03)	(6.62)	(5.03)	(−17.84)	(−2.37)
	$\log K_1K_2$	13.88	18.14	16.27	20.59	17.47	−8.59	19.89
		(10.64)	(18.13)	(16.25)	(20.57)	(17.48)	(−8.56)	(16.54)
Ni^{2+}	$\log K_1$	12.61	2.78	7.78	23.55	13.88	12.61	21.50
		(12.59)	(2.79)	(7.75)	(23.55)	(13.88)	(12.62)	(21.44)
	$\log K_2$	7.71	20.56	17.17	10.03	8.02	6.51	20.36
		(7.72)	(20.53)	(17.19)	(9.93)	(8.01)	(6.52)	(20.34)
	$\log K_1K_2$	20.32	23.34	24.92	30.76	24.62	19.15	41.79
		(20.30)	(23.36)	(24.91)	(30.75)	(24.62)	(19.14)	(41.78)
Mn^{2+}	$\log K_1$	5.73	6.57	0.64	3.08	3.22	4.36	4.43
		(5.87)	(6.55)	(0.65)	(3.08)	(3.21)	(4.35)	(4.44)
	$\log K_2$	2.15	5.60	−4.16	−1.21	−2.03	0.34	−1.07
		(1.36)	(1.39)	(−4.96)	(−1.98)	(−2.76)	(0.42)	(−1.78)
	$\log K_1K_2$	10.46	7.95	−4.36	1.07	0.44	3.96	2.65
		(10.48)	(7.98)	(−4.35)	(1.10)	(0.45)	(3.96)	(2.66)

The log K_1 and log K_2 values (Table 1) for metal complexes examined here show on comparison the order of stability of

$$Mn^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This finding is in agreement with that of Irving and Williams[7]. Table 1 shows, that the values of log K_1/K_2 are positive in all cases. No linear relationship was observed between the log K_1 of a series of metal complexes derived from one metal ion with a set of closely related ligands. The typical plots of pKa versus the log K_1 for Cu^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+} show that deviations from a straight line are of considerable magnitude for at least two ligands. The lack of correlation may be due to the steric hinderance of the *ortho* substituents.

From Table 3 it is evident that the reactions of Cu^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+} with all hydroxamic acids (II) are exothermic. It is seen from Table 4 that in most of the systems, entropy changes (ΔS°) are positive. The reaction between hydroxamic acid anion and cation would result in a decrease of the number of free charged ions in solution; as a result of this, the entropy term strongly favours complex formation[8].

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REFERENCES

1 Y. K. Agrawal and S. G. Tandon, *J. Inorg. Nucl. Chem.*, 36 (1974) 869.
2 A. I. Vogel, *A Textbook of Quantitative Inorganic Analysis*, Longmans, London, 1961.
3 F. J. Welcher, *The Analytical Uses of Ethylenediaminetetraacetic Acid*, Van Nostrand, New York, 1965.
4 A. Weissberger, *Technique of Organic Chemistry*, Vol. VII, Wiley Interscience, New York, 1955.
5 Y. K. Agrawal and S. G. Tandon, *J. Inorg. Nucl. Chem.*, 34 (1972) 1291.
6 Y. K. Agrawal, S. K. Sant and T. R. Jagdeesh, *Convention of Chemist*, Indian Chemical Society Madurai, 1974, p. 00C.
7 H. Irving and R. J. P. Williams, *Nature*, 162 (1948) 746.
8 R. J. P. Williams, *Proc. Symp. Chem.*, Danish Chemical Society, Copenhagen, 1954, p. 65.