Thermochimica Acta, 185 (1991) 263–269
Elsevier Science Publishers B.V., Amsterdam

Investigation of complexation equilibria and evaluation of thermodynamic parameters of complexes of bivalent metal ions with 2,4-pentanedione-1-(3-chlorophenylhydrazone), PD3CPH

B.S. Garg [1], Seema Walia and V.K. Jain

Department of Chemistry, University of Delhi, Delhi-110007 (India)

(Received 7 December 1990)

Abstract

Thermodynamic stability constants of the complexes of various dipositively charged metal ions, UO_2(II), Cu(II), Zn(II), Cd(II), Ni(II), Co(II) and Mn(II), with 2,4-pentanedione-1-(3-chlorophenylhydrazone) have been determined potentiometrically, in 50% (v/v) dioxan–water medium, at different temperatures and ionic strengths. The stability constants and $S_{\min}$ values have been calculated at different ionic strengths and temperatures. The method of Bjerrum and Calvin, as modified by Irving and Rossotti, has been used to find out the values of $\bar{n}$ and pL. The thermodynamic parameters ΔG, ΔH and ΔS have also been evaluated from temperature-dependent data.

INTRODUCTION

Metal complexes of aryl hydrazines and hydrazones have attracted considerable interest as antitubercular agents [1] and potential inhibitors of DNA synthesis and cell growth in a number of human and rodent cell lines grown in culture [2]. Substituted hydrazones have remarkable anticancer [3], antibacterial [3] and antileukemic [4] activity, which has since been shown to be related to their metal complexing ability.

The hydrazones offer varied bonding and stereochemical possibilities. A review on the coordination chemistry of acyl, aroyl and heteroaroyl hydrazones has been published by Dutta and Hussain [5]. In view of the significant biological activity and chelating power of hydrazones, the present study was undertaken to determine the stability constants of complexes of bivalent metal ions with 2,4-pentanedione-1-(3-chlorophenylhydrazone) (PD3CPH) at various ionic strengths and various temperatures in 50% (v/v) dioxan medium.

---

[1] Author to whom all correspondence should be addressed.

0040-6031/91/$03.50

EXPERIMENTAL

Instrumental

A digital pH-meter (model PHM83; Radiometer, Copenhagen) in conjunction with a single glass–calomel electrode was used for pH measurements. The meter was standardised with standard Radiometer buffer solutions of pH 4 and pH 7 before performing the titrations.

Chemicals and reagents

2,4-Pentanedione-1-(3-chlorophenylhydrazone) was synthesised by diazotisation of a cooled (0 ° C) hydrochloric acid solution of *m*-chloroaniline (0.1 mol) and coupling it with acetylacetone (0.1 mol) in a water–acetone mixture containing crystalline sodium acetate. The temperature was kept between 0 and 5 ° C throughout the reaction. The crude product so obtained was filtered off and recrystallised from methyl alcohol to give fine yellow needles (m.p. = 95 ° C). The purity of the product, PD3CPH, was checked by TLC and characterised by UV, IR and ^{1}H NMR spectroscopy and elemental analysis. All the metal ion solutions were prepared from their corresponding sulphates or nitrates (AR, BDH) and standardised by conventional methods. The ligand solution was prepared in 100% dioxan purified by the method of Weissberger et al. [6]. $NaClO_4$ (Fluka) was used to maintain constant ionic strength. A freshly prepared solution of tetramethylammonium hydroxide (TMAH; Merck) in 50% aqueous dioxan was used as titrant. The potentiometric titrations were carried out in a covered double-walled glass cell in a nitrogen atmosphere (N_2 purity $\approx 99\%$), which was presaturated with 50% (v/v) aqueous dioxan.

The following solution mixtures were titrated against standard 0.1 M TMAH in 50% (v/v) dioxan–H_2O

(i) 2.5 ml $HClO_4$ (0.02 M) + 2.0 ml $NaClO_4$ (1.0 M) + 0.5 ml K_2SO_4 or KNO_3 (0.02 M) + 5.0 ml H_2O + 10.0 ml dioxan;
(ii) 2.5 ml $HClO_4$ (0.02 M) + 2.0 ml $NaClO_4$ (1.0 M) + 0.5 ml K_2SO_4 or KNO_3 (0.02 M) + 5.0 ml H_2O + 10.0 ml ligand (0.01 M) in 100% dioxan;
(iii) 2.5 ml $HClO_4$ (0.02 M) + 2.0 ml $NaClO_4$ (1.0 M) + 0.5 ml metal sulphate or nitrate (0.02 M) + 5.0 ml H_2O + 10.0 ml ligand (0.01 M).

In other sets, $NaClO_4$ was added in requisite amounts to maintain the ionic strength at 0.2, 0.05 or 0.02 M.

In order to determine the thermodynamic parameters, the titrations were also performed at various temperatures: 20, 27, 35 and 45 ± 0.5 ° C. In all the titrations, temperature was maintained constant (±0.05 ° C) using a Julabo F20 thermostat (Germany) which also had a low temperature facility.

Volume corrections were applied according to the method of Rao and Mathur [7] and the pH values in aqueous organic mixtures were corrected using the method of Van Uitert and Hass [8].

From the titration curves of solution mixtures (i), (ii) and (iii) the parameters $\bar{n}_H$, the average number of protons bound to ligand, $\bar{n}$, the average number of ligand molecules bound per metal ion and pL, the free ligand exponent, were determined using the expression described by Irving and Rossotti [9,10] in order to evaluate the pK_a values of the ligand and the stability constants of the complexes. These were calculated using a weighted least-squares programme based on that of Sullivan et al. [11], computed on an Uptron PC plus computer, which determines that set of β_n values which makes the function

$$U,\left\{U = \sum_{n=0}^{N} (y - x - nz)\beta_n X^n\right\}$$

nearest to zero by minimising S

$$\left\{S = \sum_{i=1}^{I} W_i U^2(x_i, y_i, z_i)\right\}$$

with respect to variation in β_n. The $S_{\min}$ values are reported for different metal complexes; $S_{\min}$ has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined in accordance with Rydberg and Sullivan [12]. The $S_{\min}$ can be equated to χ^2.

RESULTS AND DISCUSSION

The dissociation constant of the ligand and stability constants of its complexes with metal ions were evaluated at four different ionic strengths (0.2, 0.1, 0.05 and 0.02 M $NaClO_4$) at 35 °C and at four temperatures (20, 27, 35 and 45 ± 0.5 °C) at 0.1 M $NaClO_4$ ionic strength.

The order of stability constants for the metal complexes of PD3CPH was found to be UO_2(II) > Cu(II) > Zn(II) > Cd(II) > Ni(II) > Co(II) > Mn(II), which is in good agreement with the order observed by Mellor and Maley [13] and by Irving and Williams [14,15]. The log K_1 and $S_{\min}$ values are summarised in Tables 1 and 2.

Effect of ionic strength

The values of dissociation constants of the ligand (pK_a) have been found to decrease with increasing ionic strength of the medium (Table 1) in agreement with the Debye–Huckel equation [16]

$$pK_a^{\circ} - \left[A(\mu)^{\frac{1}{2}}/1 + \alpha(\mu)^{\frac{1}{2}}\right] + C\mu = pK_a$$

A similar variation has been observed in the case of stability constants of complexes of the ligand with various metal ions.

TABLE 1

Stability constants of bivalent metal complexes of PD3CPH at different ionic strengths (μ, M) of $NaClO_4$ (temperature = 35 ± 0.5 °C)

System	Stability constant	Ionic strength			
		0.02	0.05	0.1	0.2
PD3CPH	pK_a	11.56	11.42	11.27	11.14
UO_2(II)-PD3CPH	log K_1	9.88	9.66	9.28	9.16
	log K_2	8.91	8.66	8.40	7.99
	S_{min}	0.080	0.011	0.018	0.073
Cu(II)-PD3CPH	log K_1	8.03	7.95	7.73	7.63
	log K_2	8.01	7.86	7.65	7.53
	S_{min}	0.012	0.012	0.010	0.010
Zn(II)-PD3CPH	log K_1	6.86	6.72	6.66	6.51
	S_{min}	0.096	0.090	0.050	0.099
Cd(II)-PD3CPH	log K_1	6.61	6.40	6.27	6.14
	S_{min}	0.024	0.027	0.082	0.026
Ni(II)-PD3CPH	log K_1	6.01	5.71	5.57	5.31
	log K_2	5.80	5.25	5.09	4.57
	S_{min}	0.030	0.073	0.023	0.099
Co(II)-PD3CPH	log K_1	5.82	5.53	5.40	5.18
	log K_2	5.53	5.23	4.97	4.33
	S_{min}	0.032	0.027	0.023	0.049
Mn(II)-PD3CPH	log K_1	5.63	5.34	5.01	4.73
	log K_2	5.42	4.97	4.55	4.25
	S_{min}	0.079	0.058	0.071	0.064

Effect of temperature

The present investigations have clearly shown that the stability constants decrease with increase in temperature, along with the pK_a values (Table 2). These results are in good agreement with those of Pitzer [17].

The thermodynamic parameters ΔG, ΔH and ΔS were also evaluated using the following relationships:

$$\Delta G = -RT \ln K$$

$$d \log K/d(1/T) = \Delta H/2.303K$$

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

The overall free energy, enthalpy and entropy changes are reported in Table 2.

Thermodynamic stability constants obtained by extrapolating the straight line plots of log K vs. $(\mu)^{1/2}$ to zero ionic strength are given in Table 3, along with the thermodynamic stabilization energy δH. The δH and E_r(Mn – Zn) values have been calculated according to the method of George and

TABLE 2

Stability constants of complexes of bivalent metals with PD3CPH at $\mu = 0.1$ M $NaClO_4$ at different temperatures and their thermodynamic parameters at $\mu = 0.1$ M $NaClO_4$ and temperature = 35 ± 0.5 °C

System	Stability constant	20 ± 0.5 °C	27 ± 0.5 °C	35 ± 0.5 °C	45 ± 0.5 °C	$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
PD3CPH	pK_a	11.58	11.44	11.27	11.16			
UO_2(II)–PD3CPH	log K_1	9.65	9.55	9.28	8.95			
	log K_2	8.84	8.56	8.40	8.38			
	S_{min}	0.010	0.008	0.018	0.004	54.29	28.63	0.732
Cu(II)–PD3CPH	log K_1	8.00	7.90	7.73	7.59			
	log K_2	7.68	7.85	7.65	7.48			
	S_{min}	0.082	0.025	0.010	0.015	45.22	29.97	0.435
Zn(II)–PD3CPH	log K_1	6.91	6.74	6.66	6.52			
	S_{min}	0.083	0.029	0.050	0.021	38.95	24.41	0.415
Cd(II)–PD3CPH	log K_1	6.65	6.53	6.27	6.19			
	S_{min}	0.060	0.045	0.082	0.037	36.70	27.08	0.274
Ni(II)–PD3CPH	log K_1	6.37	6.09	5.57	5.38			
	log K_2	5.50	5.48	5.09	5.00			
	S_{min}	0.057	0.063	0.023	0.061	33.18	57.30	−0.689
Co(II)–PD3CPH	log K_1	5.99	5.53	5.40	5.23			
	log K_2	5.37	5.43	4.97	4.81			
	S_{min}	0.060	0.018	0.023	0.011	31.60	50.41	−0.537
Mn(II)–PD3CPH	log K_1	5.55	5.21	5.01	4.87			
	log K_2	5.08	5.00	4.55	4.55			
	S_{min}	0.080	0.014	0.071	0.021	29.30	43.51	−0.406

TABLE 3

E_r(Mn – Zn) and δH values for complexes of PD3CPH

Parameter	Metal ion				
	Mn^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}	Cu^{2+}
log $K_1°$	5.98	6.16	6.38	7.02	8.20
ΔF	34.98	36.03	37.32	41.08	47.98
ΔF_R	–	1.04	2.34	6.10	12.99
ΔH_H	–	179.95	259.47	196.69	263.65
ΔH_L	–	180.99	261.81	202.79	276.64
$(n-5)/5\ E_r$	–	81.00	121.51	–	162.01
δH	–	49.99	140.30	–	114.63

Key: ΔF = free energy change on complexation = 2.303RT log $K_1°$, where R, T and $K_1°$ have the usual significance, temp. = 303 K; ΔF_R = change in heat content for the formation of the complex in solution relative to Mn^{2+}; ΔH_H = heat of hydration of metal ions relative to Mn^{2+}; ΔH_L = heat of complexation referred to the metal ion in gaseous and ligand in solution state; n = number of electrons in 3d orbital; $(n-5)/5\ E_r$ = lattice energy difference for Zn^{2+} and Mn^{2+} complexes; δH = thermodynamic stabilization energy; log $K_1°$ = values obtained by extropolating the log K_1 vs. $\mu^{1/2}$ plot to zero ionic strength (heat units are in kJ mol^{-1}).

McClure [18] and are listed in Table 3. The hydration energies used are those given by George and McClure [18]. The order of δH is

Co < Ni > Cu

The above results indicate that the complexation reactions are spontaneous. The entropy is, however, negative for Ni(II), Co(II) and Mn(II), showing that entropy is not favourable for their complexation reactions.

REFERENCES

1 E. Sorkin, W. Roth and H. Erlenmeyer, Helv. Chim. Acta, 35 (1952) 1736.

2 D.K. Johnson, T.B. Murphy, N.J. Rose, W.H. Goodwin and L. Pickart, Inorg. Chim. Acta, 67 (1982) 159.

3 M.A. Chernyavskaya, L.A. Smirnova, A.S. Belova, Yu.A. Davidovich, K.K. Babievskii and S.V. Rogozhir, Chem. Abstr., 107 (1987) 194800*g*.

4 R. Braun, W. Dittmar and D. Gouicka, Naturwissenschaften, 65 (1978) 267.

5 R.L. Dutta and Md.M. Hussain, J. Sci. Ind. Res., 44 (1985) 635.

6 A. Weissberger, E.S. Proskauer, J.A. Riddick and E.E. Topps, Jr., Techniques of Organic Chemistry, Interscience, New York, 1955, p. 7.

7 U.B. Rao and H.B. Mathur, Indian J. Chem., 7 (1969) 1234.

8 L.G. Van Uitert and C.G. Hass, J. Am. Chem. Soc., 75 (1953) 451.

9 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1953) 3397.

10 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.

11 J.C. Sullivan, J. Rydberg and W.E. Miler, Acta Chem. Scand., 13 (1959) 2023.

12 J. Rydberg and J.C. Sullivan, Acta Chem. Scand., 13 (1959) 2059.

13 D.P. Mellor and L. Maley, Nature (London), 161 (1948) 436.
14 H.M. Irving and R.J.P. Williams, Nature (London), 162 (1948) 746.
15 H.M. Irving and R.J.P. Williams, J. Chem. Soc., (1953) 3192.
16 R. Nasanen and A. Ekman, Acta Chem. Scand., 6 (1952) 1389.
17 K.S. Pitzer, J. Am. Chem. Soc., 50 (1937) 2365.
18 P. George and D.S. McClure, Prog. Inorg. Chem., 1 (1959) 428.