Thermochimica Acta, 55 (1982) 125–133
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

INNER ORBITAL SPLITTING IN SOME $3d^n$ TRANSITION METAL COMPLEXES WITH OXYGEN, SULPHUR AND NITROGEN DONOR LIGANDS

P.C. SRIVASTAVA

Physical Research Wing, Fertilizer (P and D) India Ltd., Sindri 828122 (India)

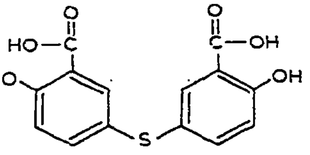
(Received 14 October 1981)

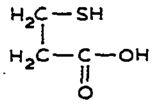
ABSTRACT

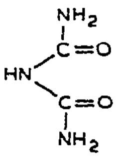
The thermodynamic equilibrium constants of the $3d^n$ transition metals [Zn^{2+}($3d^{10}$), Cu^{2+}($3d^9$), Ni^{2+}($3d^8$), Co^{2+}($3d^7$), and Mn^{2+}($3d^5$)] complexes with the oxygen donor ligand 5,5'thiodisalicylic acid ($TDSH_4$) and sulphur donor ligand α-mercaptopropionic acid (MPA) have been determined potentiometrically at 35±0.1°C. The thermodynamic parameters ΔG, ΔH and ΔS have been calculated. The nitrogen donor ligand biuret (BT) has been included here for comparative studies of the complexing behaviour. The transition series contraction energy E_r (Mn–Zn) and thermodynamic ligand field stabilization energy "δH" of the metal complexes have been evaluated. The inner orbital splitting values of the complexes show the order for the ligand activity to be BT>$TDSH_4$>MPA≃H_2O.

INTRODUCTION

The equilibrium constants and thermodynamic ligand field parameters have an immense importance in analytical chemistry. Some studies on transition metal complexes and analytical behaviour of 5,5′-thiodisalicylic acid ($TDSH_4$) [1–5] [$C_6H_3(OH)COOHSC_6H_3(OH)COOH$, structure I], α-mercaptopropionic acid (MPA) [6,7], ($HSCH_2CH_2COOH$, structure II) have been reported earlier. The industrially important ligand Biuret (BT) [8–12] ($H_2NCONHCONH_2$, structure III) has been included here for comparative studies of the complexing behaviour and inner orbital splitting of the $3d^n$ transition metal complexes. The stability constants and other relevant thermodynamic parameters of the BT complexes have been studied by us [13].


TDSH$_4$
(I)


MPA
(II)


BT
(III)

In the present paper, stability constants and thermodynamic parameters of Zn^{2+},

0040-6031/82/0000-0000/$02.75 © 1982 Elsevier Scientific Publishing Company

Cu^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} with $TDSH_4$ and MPA have been studied at 35 ± 0.1°C. An attempt has been made to calculate the contraction energy of the transition series and the thermodynamic ligand field stabilization energy of $3d^n$ metal complexes and their results have been discussed.

EXPERIMENTAL

The stability constants of BT [13] at 25°C and 35°C and $TDSH_4$ [5] and MPA [6] at 25°C with $Zn^{2+}(3d^{10})$, $Cu^{2+}(3d^9)$, $Ni^{2+}(3d^8)$, $Co^{2+}(3d^7)$ and $Mn^{2+}(3d^5)$ ions have been reported by Srivastava et al.

All the titrations of the $TDSH_4$ and MPA complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions at 35° ± 0.1°C were carried out using CO_2 free 0.1 M NaOH. Solutions were brought to 0.1 M ionic strength by addition of the requisite amount of $KClO_4$. The final volume of titrant mixture [mixture I, $HClO_4$ (0.02 M); mixture II, $HClO_4$ (0.02 M) + ligand (0.01 M); and mixture III, $HClO_4$ (0.02 M) + ligand (0.01 M) + metal solution (0.05 M); (where ligand stands for $TDSH_4$ or MPA)] was adjusted to 50 ml. Nitrogen gas was bubbled through the solution to provide an inert atmosphere.

The hydrogen ion concentration was measured using a Phillips pH meter with a glass calomel electrode assembly at a constant temperature of 35 ± 0.1°.

CALCULATIONS AND RESULTS

The nature of the titration curves obtained is similar to that reported earlier [5,6]. The $\bar{n}_H$, $\bar{n}$ and p_L were calculated by using the relationship derived by Irving and Rossotti [14]. A plot of the degree of formation, $\bar{n}_H$, of the proton vs. pH was used for the estimation of the proton–ligand stability constant (pK) with the aid of Bjerrum half integral method [15]. The estimated pK values are given in Table 1 along with values at 25°C. The metal–ligand formation curves was obtained by plotting $\bar{n}$ vs. p_L. The metal–ligand stability constants were obtained by using point wise calculation and a graphical method [14]. The stability constants and overall stability constants (log β) along with the values at 25°C are reported in Table 1.

To determine the values of overall changes in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) the well known temperature coefficient equation and the Gibbs–Helmhotz equation were employed, viz.

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

$$\Delta H = \frac{2.303 RT_1T_2(\log K_2 - \log K_1)}{T_2 - T_1}$$

and

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

TABLE 1

Protonation constants of the ligands stepwise and over all stability constants and thermodynamic parameters of the metal complexes with $TDSH_4$ and MPA

Metal ion	Protonation constants stability constants	Temperature at 25°C		Temperature at 35°C		$-\Delta G$ (kcal $mole^{-1}$)				ΔH at 35° (kcal $mole^{-1}$)		ΔS (cal $mole^{-1}$)	
		$TDSH_4$ [a]	MPA [b]	$TDSH_4$	MPA	at 25°		at 35°		$TDSH_4$	MPA	$TDSH_4$	MPA
						$TDSH_4$ [a]	MPA [b]	$TDSH_4$	MPA				
	pK_1	3.65	4.2	3.95	4.65								
	pK_2	4.55	10.8	4.80	11.10								
	pK_3	12.20		12.60									
	pK_4	12.90		13.20									
Mn^{2+}	$\log K_1$	7.30	5.70	7.75	6.30	9.86	7.70	10.54	8.57	18.87	25.16	27.04	53.86
	$\log K_2$	3.10		3.45		4.20		4.69		14.68		32.44	
	$\log \beta$	10.40	5.70	11.20	6.30	14.06	7.70	15.23	8.57	33.55	25.16	59.48	52.86
Co^{2+}	$\log K_1$	8.33	5.80	8.80	6.45	11.26	7.84	11.97	8.78	19.71	27.26	25.13	60.00
	$\log K_2$	3.45		3.75		4.79		5.10		12.58		24.28	
	$\log \beta$	11.78	5.80	12.55	6.45	16.05	7.84	17.08	8.78	32.39	27.26	49.41	60.00
Ni^{2+}	$\log K_1$	8.34	8.25	8.25	8.55	11.28	11.15	12.05	11.64	21.38	12.58	30.29	3.05
	$\log K_2$	3.53	3.10	3.95	3.40	4.87	4.29	5.27	4.60	17.62	12.58	39.77	25.90
	$\log \beta$	11.87	11.35	12.80	11.95	16.15	15.45	17.42	16.24	39.00	25.16	70.06	28.95
Cu^{2+}	$\log K_1$	9.05	6.55	9.60	6.95	12.23	8.85	13.06	9.46	23.06	16.77	32.48	23.73
	$\log K_2$	3.10	2.45	3.55	2.70	4.30	3.40	14.83	3.67	18.87	10.48	45.58	22.11
	$\log \beta$	12.15	9.00	13.15	9.65	16.53	12.25	17.89	13.13	41.93	27.25	78.04	45.84
Zn^{2+}	$\log K_1$	7.40	8.05	7.85	8.40	10.01	10.87	10.68	11.43	18.87	14.68	26.59	10.55
	$\log K_2$	3.54	3.15	3.95	3.45	4.88	4.37	5.37	4.69	17.19	12.58	38.37	25.61
	$\log \beta$	10.94	11.20	11.80	11.85	14.89	15.24	16.05	16.12	36.06	27.26	64.96	36.16

[a] The stability constants values are taken from ref. 5.

[b] The stability constants values are taken from ref. 6.

where R is the gas constant, T_1 and T_2 are the temperatures in absolute degrees and log K_1 and log K_2 are constants at T_1 and T_2, respectively. Table I incorporates the thermodynamic parameters.

THERMODYNAMIC LIGAND FIELD STABILIZATION ENERGY

The contraction energy of the transition series (E_r) [$3d^5$–$3d^{10}$] is a function of the temperature coefficient of the reaction i.e. the energy change

$$Zn^{2+}(q) + MnX^{2+}(n\ aq) \rightarrow ZnX^{2+}(n\ aq) + Mn^{2+}(g)$$

So the E_r value is a measure of the influence on the ligand of the greater effective ionic charge of $Zn^{2+}(d^{10})$ ion relative to $Mn^{2+}(d^5)$ and is expressed by the equation

$$E_r = -[\Delta H_L(Zn^{2+})] + (Mn^{2+})\,\Delta H_L \qquad (1)$$

where

$$\Delta H_L(M^{2+}) = \Delta H_{Hr}(M^{2+}) + \Delta H_c(M^{2+}) \qquad (2)$$

and

$$E_r = -[\Delta H_{Hr}(Zn^{2+}) + \Delta H_c(Zn^{2+})] + [\Delta H_{Hr}(Mn^{2+}) + \Delta H_c(Mn^{2+})] \qquad (3)$$

Here $\Delta H_{Hr}(M^{2+})$ [M = Zn, Cu, Co or Ni] is the relative value for Mn^{2+} of the hydration energy of the transition metal ions (ΔH_H), viz. $M^{2+}(g) \rightarrow M^{2+}(aq)$ and ΔH_c is the relative value for Mn^{2+} of the free energy change (ΔG) of the complexes. The value of hydration energy, ΔH_H are those given by George and McClure [16].

If it is assumed that all the complexes [$Mn^{2+}(d^5)$–$Zn^{2+}(3d^{10})$] have the same symmetry, viz. six coordination (octahedral) or four coordination (tetrahedral/square planar), the thermodynamic ligand field stabilization energy (LFSE), "δH", in

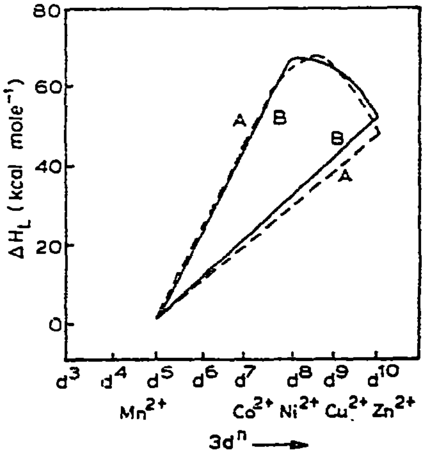


Fig. 1. Plot of ΔH_L vs. $3d^n$ for A, TDSH$_4$ and B, MPA.

TABLE 2

Thermodynamic ligand field stabilization energy (δH) and ($10 Dq$) of $3d^n$ divalent metal complex with 5,5′-thiodisalicylic acid

Metal ion	ΔH_H (kcal mole^{-1})	ΔH_{Hr} (kcal mole^{-1})	ΔH_c (kcal mole^{-1})	ΔH_L (kcal mole^{-1})	E_r (Zn–Mn)	λE_r	δH (kcal mole^{-1})	$10 Dq$ (cm^{-1}) solution	$10 Dq$ (cm^{-1}) optical[a] data	LFSE (kcal mole^{-1}) optical data	$10 Dq$ (cm^{-1}) aquo[b] complex	LFSE (kcal mole^{-1}) aquo complex	LFSE M^{2+} (TDSH$_4$) / LFSE M^{2+} (aquo)
$Mn^{2+}(3d^5)$	654												
$Co^{2+}(3d^7)$	697	43	1.86	44.86	47.74	19.10	25.76	15,060	11,100	18.99	14,000	23.94	1.08
$Ni^{2+}(3d^8)$	716	62	1.98	63.98		28.64	35.34	10,330	10,000	34.2	10,000	34.20	1.03
$Cu^{2+}(3d^9)$	717	63	2.37	65.37		38.20	27.10	15,890	13,890	23.7	15,000	25.65	1.05
$Zn^{2+}(3d^{10})$	707	47.1	0.74	47.74									

[a] Optical values are taken from refs. 18 and 19.

[b] The values of 10 *Dq* of aquo complexes are taken from ref. 20.

TABLE 3

The thermodynamic LFSE (δH), and 10 Dq of $3d^n$ divalent transition metal interaction with α-mercaptopropionic acid

Metal ion	ΔH_C (kcal mole^{-1})	ΔH_L (kcal mole^{-1})	E_r	λE_r	δH (kcal mole^{-1})	10 Dq (cm^{-1})	10 Dq (cm^{-1}) optical data[a]	L.F.S.E. (kcal mole^{-1}) optical data	$\dfrac{\text{LFSE M}^{2+}\text{ (MPA)}}{\text{LFSE M}^{2+}\text{ (aquo)}}$
Mn^{2+}									
Co^{2+}	0.14	43.14		20.04	23.10	13,500	10,500	18.04	0.97
Ni^{2+}	3.45	65.45	50.10	30.06	35.39	10,350	9,600	32.53	1.03
Cu^{2+}	1.15	64.15		40.08	24.07	14,070	15,200	27.00	0.94
Zn^{2+}	3.17	50.17							

[a] The optical data are taken from ref. 7.

TABLE 4

Thermodynamic ligand field stabilization energy (δH)[a], and LFSE (optical) of the Biuret complexes

Metal ion	δH[a] (kcal mole^{-1})	LFSE (kcal mole^{-1}) optical data	10 Dq[b] (cm^{-1}) optical data	$\frac{\text{LFSE M}^{2+}\text{(BT)}}{\text{LFSE M}^{2+}\text{(aquo)}}$
Co^{2+}	35.42	15.39	9000	1.48
Ni^{2+}	45.12	28.93	8460	1.32
Cu^{2+}	38.12	22.05	12900	1.44

[a] δH values are taken from ref. 13.

[b] The value of 10 Dq and LFSE are calculated from the optical data [8,12].

complexes of $3d^n$ metal ion M^{2+} may be expressed by

$$\delta H = (\Delta H_L)d^n - \lambda E_r \tag{4}$$

where λ is a constant and depends upon the number of electrons in the $3d$ orbital ($\lambda = 0.4$ for d^7, 0.6 for d^8 and 0.8 for d^9 configurations).

The plot of ΔH_L of the complexes as a function of the number of $3d^n$ electrons in metal ions is shown in Fig. 1. The transition series contraction energy (E_r) evaluated from the plots are found to be 47.74 and 50.10 kcal mole^{-1} for $TDSH_4$ and MPA complexes, respectively. The values of δH of the complexes as calculated from eqn. (4) are given in Tables 2 and 3 for the respective ligands. The ligand field stabilization energy of Biuret complexes [13] is also shown here (Table 4) for comparison.

DISCUSSION

It is observed from the stepwise stability constant data, Table 1, that in all the systems log K_1 (first equilibrium constant) > log K_2 (second equilibrium constant). The overall stability constant of $TDSH_4$–metal complexes follow the order; $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ which agrees with Irving and Williams' order [17] for the bivalent $3d^n$ transition metal series. However in the case of the MPA complex the sequence order is $Mn^{2+} < Co^{2+} < Ni^{2+} > Cu^{2+} > Zn^{2+}$, which does not conform with the Irving–Williams order. The unexpectedly low value of Cu^{2+} is due to the reduction of $Cu^{2+}(3d^9)$ to $Cu^{1+}(3d^{10})$ by the SH group [6] present in MPA. The complexes of bivalent metal ions with $TDSH_4$ and MPA are formed spontaneously as shown by the negative values of the free energy change (Table 1). The value of the enthalpy change in all cases is positive, which explains the increase in values of the formation constant with the rise in temperature. The positive value of ΔS in all cases indicates that the complex formation is favoured by an increase in entropy of the system.

The values of the thermodynamic ligand field stabilization energy "δH" of the bivalent transition metal ions with the oxygen donor ($TDSH_4$), sulphur donor

(MPA) and nitrogen donor (BT) follow the order; $Ni^{2+} > Cu^{2+} > Co^{2+}$. The low value of Cu^{2+} confirms the steric hindrance which prevents the formation of a four-coordinated structure. In the case of $Cu^{2+}(3d^9)$, a stabilization energy of $\Delta^{\text{complex}}_{\text{ligand}} = -6\,[Dq(\text{L}) - Dq(\text{H}_2\text{O})]$ is expected here; however, special effects appear, as copper complexes display strong Jahn–Teller distortion. Such an effect is accompanied by a decrease in the stabilization energy. A more quantitative comparison can be made of δH and LFSE values with those calculated from the available optical data (10 Dq) (where Dq is spectroscopic splitting factor) of the $TDSH_4$ [18,19], MPA [7] and BT [8,12] and aquo [20] complexes. The ligand field stabilization energy LFSE, from the published optical data is calculated by multiplying Dq by the appropriate factors (LFSE optical $= 2.85 \times n \times Dq$; where $n = 6$ for $3d^9$ and $3d^7$ and 12 for $3d^8$ configuration in a weak field of D_{4h} symmetry). These values are given in the respective table along with "10 Dq" values for comparison. The LFSE values from optical data follow the same sequence order as δH values. The δH values of the $TDSH_4$, MPA and BT complexes are more than the LFSE values calculated from optical data. The higher values reveal that some extra stabilization is present in these complexes over and above that estimated from optical stabilization energy. The ratio of LFSE (M^{2+}L) (where L stands for $TDSH_4$, MPA and BT) to LFSE (M^{2+}aq) of $TDSH_4$, MPA and BT is ~ 1.15, 1 and 1.4. The value of ΔH for the BT complexes are more comparable with those for $TDSH_4$ and MPA complexes. The δH and 10 Dq values of MPA and aquo complexes indicate that the COOH and SH groups of the MPA and H_2O molecules make a very similar contribution to the ligand field. With $TDSH_4$, even though two COOH and OH groups are bonded to the metal ions, forming six-membered rings, the value of δH for Co^{2+}, Ni^{2+} and Cu^{2+} complexes are more than the value for the water molecule.

For the values of 10 Dq or δH produced with the given bivalent metal ions, the coordination ability of the above mentioned ligands may be placed in the order $BT > TDSH_4 > MPA \simeq H_2O$.

ACKNOWLEDGEMENT

I would like to thank Sri K.C. Banerjee, Senior Manager (P.R.W.) for his keen interest in the present investigation.

REFERENCES

1 J.S. Elliot and E.D. Edward, U.S. Pat. 2,820,766 (1958); Chem. Abstr., 52 (1958) 8540i.
2 E.A. Evans and J.S. Elliot, U.S. Pats. 2,388,047 (1945); 2,692,859 (1956).
3 S.C. Srivastava and M.L. Good, Talanta 12 (1965) 181.
4 P.C. Srivastava, S. Prakash and H.L. Nigam, Indian J. Chem., 9 (1971) 1289.
5 A.N. Kumar, P.C. Srivastava and H.L. Nigam, Indian J. Chem., 2 (1971) 488.
6 S.K. Srivastava, P.C. Srivastava and H.L. Nigam, Indian J. Chem., 10 (1972) 223.
7 S.K. Srivastava, D. Phil. Thesis, Allahabad University, 1973.

8 A.W. Mclellan and G.A. Melson, J. Chem. Soc. A, (1967) 137.
9 F. Kurzer. Chem. Rev., 56 (1956) 95.
10 R.M. Sanyal, P.C. Srivastava and B.K. Banerjee, Technology, 11 (1974) 258.
11 R.M. Sanyal, P.C. Srivastava and B.K. Banerjee, J. Inorg. Nucl. Chem., 37 (1975) 343.
12 J.J. Bour. P.J.M.W.L. Birker and J.J. Steggered. Inorg. Chem., 10 (1971) 1202. G.A. Melson. J. Chem. Soc. A, (1967) 669.
13 P.C. Srivastava and B.K. Banerjee. Indian J. Chem., 17A (1979) 583.
14 H. Irving and H.S. Rossotti. J. Chem. Soc., (1953) 3397.
15 J. Bjerrum. Metal Amine Formation in Aqueous Solution. Hasse. Copenhagen, 1942.
16 P. George and D.S. McClure, Prog. Inorg. Chem., 1 (1959) 381.
17 H. Irving and R.J.P. Williams, Nature (London), 162 (1948) 746.
18 P.C. Srivastava, K.B. Pandeya and H.L. Nigam, J. Inorg. Nucl. Chem., 35 (1973) 3613.
19 P.C. Srivastava, D. Phil. Thesis, Allahabad University, 1971.
20 B.N. Figgis, Introduction to Ligand Fields, Interscience, New York, 1964, p. 74.