Thermochimica Acta, 72 (1984) 381–385
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

STABILITY AND THERMODYNAMICS OF La(III)-, Pr(III)-, Nd(III)-, Gd(III)- AND Eu(III)-*p*-NITROBENZALDEHYDE THIOSEMICARBAZONE SYSTEMS

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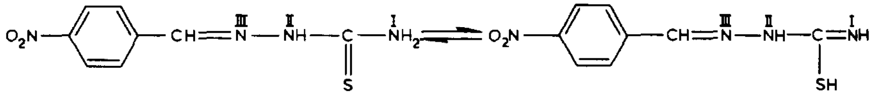
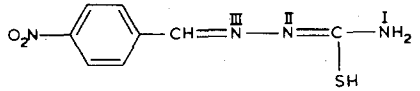
(Received 26 July 1983)

This report is a continuation of the solution studies on Cu(II)-, Ni(II)-, Co(II)-, Mn(II)- and Zn(II)-*p*-N.BzH.THSMC (*p*-nitrobenzaldehyde thiosemicarbazone) systems by Sawhney and Sati [1]. In the previous work an explanation was given of the change of the thione to the thiol form when *p*-N.BzH.THSMC undergoes tautomerism in solution; the dominating form is conjugated (=N–N=) thus



Thione form

or



Thiol form (**1a**)

This work is concerned with the stoichiometries, stability and thermodynamics of La(III)-, Pr(III)-, Nd(III)-, Gd(III) and Eu(III)-*p*-N.BzH.THSMC systems under the experimental conditions.

EXPERIMENTAL

All the chemicals used were of BDH grade. Synthesis of *p*-N.BzH.THSMC involved addition of equimolecular quantities of *p*-nitrobenzaldehyde (Koch-Light, London) in acetone and thiosemicarbazide (LOBA) in water, followed by mild shaking, filtering, washing of precipitate with water and drying at 35–40°C. Chemical analysis data were in agreement with the empirical formula: $C_8H_8N_4O_2S$. Metal solutions in water, duly standardised, were used for the present study.

0040-6031/84/$03.00

TABLE 1

Stepwise formation contants and thermodynamic functions of metal complexes of *p*-nitrobenzaldehyde thiosemicarbazone

Metal ion	Metal ligand stability constants	Method [a]	Temp.		ΔG^0 (kcal mol^{-1})		ΔH^0 (kcal mol^{-1})	ΔS^0 (cal mol^{-1} deg^{-1})
			28°C	38°C	28°C	38°C	28°C	38°C
La(III)	log k_1	A	10.85	9.40				
		B	10.83	9.46				
		C	10.85	9.44				
		Mean	10.84	9.45				
	log k_2	A	9.50	7.50				
		B	9.61	7.59				
		C	9.62	7.60				
		Mean	9.62	7.60				
	log k_3	A	7.10	5.80				
		B	6.93	5.72				
		C	7.05	5.74				
		Mean	6.99	5.73				
	logβ_3		27.45	22.78	−37.81	−32.42	−200.05	−539.00
Pr(III)	log k_1	A	11.10	10.40				
		B	11.04	10.42				
		C	–	–				
		Mean	11.04	10.42				
	log k_2	A	9.20	9.00				
		B	9.25	8.80				
		C	9.15	8.70				
		Mean	9.20	8.75				
	log k_3	A	6.90	6.00				
		B	6.87	5.95				
		C	6.84	5.92				
		Mean	6.86	5.94				
	log β_3		27.10	25.11	−37.33	−35.73	−85.24	−159.20
Nd(III)	log k_1	A	9.00	8.20				
		B	9.09	8.42				
		C	–	8.40				
		Mean	9.09	8.41				

	$\log k_2$	A	7.90	6.10			
		B	7.76	6.04			
		C	7.70	6.03			
		Mean	7.73	6.04			
	$\log k_3$	A	5.70	4.30			
		B	5.64	4.26			
		C	5.64	4.25			
		Mean	5.64	4.26			
	$\log \beta_3$		22.46	18.71	−30.94	−26.63	−160.64	−430.90
Eu(III)	$\log k_1$	A	10.80	10.15			
		A	10.80	10.15			
		B	10.80	10.23			
		C	10.90	10.30			
		Mean	10.85	10.27			
	$\log k_2$	A	8.10	8.50			
		B	8.27	8.59			
		C	8.20	8.62			
		Mean	8.24	8.61			
	$\log k_3$	A	5.90	5.10			
		B	6.06	5.63			
		C	6.10	5.45			
		Mean	6.08	5.54			
	$\log \beta_3$		25.17	24.42	−34.67	−34.75	−32.13	+08.42
Gd(III)	$\log k_1$	A	10.60	10.00			
		B	10.56	9.99			
		C	10.58	10.15			
		Mean	10.57	10.07			
	$\log k_2$	A	8.60	7.65			
		B	8.89	7.80			
		C	8.84	7.80			
		Mean	8.87	7.80			
	$\log k_3$	A	6.90	5.30			
		B	6.91	5.22			
		C	6.95	5.37			
		Mean	6.93	5.30			
	$\log \beta_3$		26.37	23.17	−36.32	−32.97	−137.08	−334.76

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[a] A = Bjerrum's half integral method; B = pointwise calculation method; C = graphical method; Mean = B and C.

pH-Metric titrations of the following solutions: (a) 4×10^{-3} M HCl, 1×10^{-1} M KCl; (b) 4×10^{-3} M HCl, 1×10^{-1} M KCl, 1×10^{-3} M *p*-N.BzH.THSMC; (c) 4×10^{-3} M HCl, 1×10^{-1} M KCl, 1×10^{-3} M *p*-N.BzH.THSMC, 2×10^{-5} M metal ion, were performed with 0.1 M NaOH (50% acetone–water) on a Beckman H-2 pH-meter equipped with a glass and calomel electrode assembly and standardised with standard buffers. pH values were corrected for volume and non-aqueous media (50% acetone–water) according to Van-Uitert and Haas [2]. The ensuing curves (pH vs. volume of NaOH) have the usual shapes.

RESULTS AND DISCUSSION

The formation function ($\bar{n}$) was computed following Bjerrum's concept [3]. Free ligand exponent (pL) was calculated corresponding to different pH values utilizing the reported values of ${}^{P}K^{H}$ ($10^{11.20}$ and $10^{10.25}$ at 28°C and 38°C) of *p*-N.BzH.THSMC by Sawhney and Sati [1] in Bjerrum's expression

$$\mathrm{pL} = \log\left[1 + (\mathrm{H}^+)^{P}K^{H}/\Delta\mathrm{NaOH}\right] \tag{1}$$

Separation of the metal titration curve from the *p*-N.BzH.THSMC curve in all the systems under study led us to believe that H^+ furnished to the solution by OH^- was removed by the formation of neutral H_2O and that the anion of *p*-N.BzH.THSMC was subsequently involved in complexation. Hydrolysis of the metal was avoided in each set by keeping a ratio of five parts of *p*-N.BzH.THSMC to one part of metal ion.

Formation curves were obtained by plotting $\bar{n}$ vs. pL; completeness was clearly shown at both ends. From these curves, the values of log ${}^{P}K^{H}$, log k_1, log k_2 and log k_3 at $\bar{n} = 0.5$, 1.5, 2.5 were read, which subsequently gave log k_1/k_2 values of less than 2.5, overruling the application of Bjerrum's half integral method for the evaluation of constants. For some systems the log k_1/k_2 value neared 2.5. However, to increase the dependence of the data, for all systems, pointwise calculation and graphical methods utilizing eqns. (2), (3) and (4) were used.

$$\log k_1 = \mathrm{pL} + \log \bar{n}/1 - \bar{n} \qquad (\bar{n} = 0\text{–}1) \tag{2}$$

$$\log k_2 = \mathrm{pL} + \log \bar{n} - 1/2 - \bar{n} \qquad (\bar{n} = 1\text{–}2) \tag{3}$$

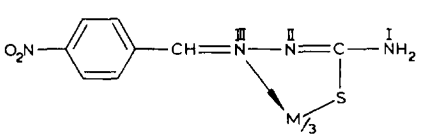
$$\log k_3 = \mathrm{pL} + \log \bar{n} - 2/3 - \bar{n} \qquad (\bar{n} = 2\text{–}3) \tag{4}$$

In Table 1 are listed the stability constants and thermodynamic functions of the systems.

Data in Table 1 show that log k_1, log k_2 and log k_3 of La(III)-, Pr(III)-, Nd(III)-, Gd(III)- and Eu(III)-*p*-N.BzH.THSMC systems decrease with increasing temperature, indicating that the low temperature is favourable for the reactions. This is because of the decrease in the number of collisions with the decrease of kinetic energy of the participating molecules; hence the lowering of stability of the systems as the temperature rises is justified. Assumption of negative values of ΔG^0 for the systems indicates that the reactions are spontaneous processes. The less negative values of ΔG^0 at the higher temperature hinted at the lessening of the reaction-feasibility as the temperature increases; only for the Eu(III)-*p*-N.BzH.THSMC system was a more negative value observed. Negative ΔH^0 values for all the systems indicate the exothermic nature of the reactions, concluding lower temperature as favourable for chelation, which agrees with the previous inferences. Complexation of La(III), Pr(III), Nd(III) or Gd(III) with *p*-N.BzH.THSMC under the experimental conditions appears to be enthalpy-controlled. Higher values of ΔH^0 hint at the considerable degree of covalency in the metal–*p*-N.BzH.THSMC chelates probably through the terminal hydrazine nitrogen N(III) atom, established by Goronback and Rasmussen [4], Beecroft et. al. [5], Ronaldhaines and Sun [6] and Malic and Phillips [7] through spectroscopic studies. Favourable entropy (ΔS^0) was only observed for the Eu(III)-*p*-N.BzH.THSMC system.

The formation function, $\bar{n}$, neared 3 in all the systems, meaning thereby that 1 : 1, 1 : 2 and 1 : 3 complexes exist in solution.

Analytical data suggest the following possible structure of metal–*p*-N.BzH.THSMC chelates



Tris(*p*-nitrobenzaldehyde thiosemicarbazonato) M(III), where M = La(III), Pr(III), Nd(III), Gd(III) and Eu(III).

ACKNOWLEDGEMENTS

The authors thank the authorities of D.A.V. (P.G.) College, Dehra Dun, India, for providing necessary facilities.

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