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Note

pH-METRIC STUDIES ON TRIS(*p*-CHLOROBENZALDEHYDE-THIOSEMICARBAZONATO)M(III) (M = Pr, Nd)

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Sawhney et al. [1–4] have investigated in depth systems consisting of a metal and a derivative of semithiosemicarbazide in solution, in order to understand their chemistry and to throw light on the carcinostatic features of these compounds. This time we have selected Pr(III)– and Nd(III)–*p*-chlorobenzaldehydethiosemicarbazone (henceforth abbreviated to p.Cl.BZH.THSMC) systems for solution pH-metric study.

EXPERIMENTAL

All chemicals used were of analytical grade. The synthesis of p.Cl.BZH.THSMC and solution study details have been reported elsewhere [3].

RESULTS AND DISCUSSION

Bjerrum's treatment [5] was adopted to calculate the formation constants of the various systems. The whole study was thermodynamically valid as the investigation was conducted at infinite dilution and constant ionic strength (0.1 N KNO_3). Values of the proton–ligand stability constant reported earlier [3] ($\log {}^{P}K^{H} = 10.25$ at 28°C and 9.70 at 38°C) were employed to calculate the metal–ligand stability constants of the systems under study.

$\bar{n}$ approached 3 in both cases at the prevailing temperatures, indicating the existence of 1 : 1, 1 : 2 and 1 : 3 complex species in solution.

The metal stability constants calculated from formation curves for each of the systems did not adhere to Bjerrum's relationship ($\log k_1/k_2 \geq 2.5$); therefore the constants had to be determined by more dependable graphical methods.

The stability data for the systems revealed a decreasing trend in the stepwise stability constants, indicating a decrease in bond strength with the successive attachment of molecules of p.Cl.BZH-THSMC ($\log k_1 > \log k_2 > \log k_3$). Further analysis hinted that higher temperatures were favourable for both reactions; this may be attributed to the increased frequency of

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TABLE 1

Stability and thermodynamic data[a] for the Pr(III)- and Nd(III)–p.Cl.BZH.THSMC systems

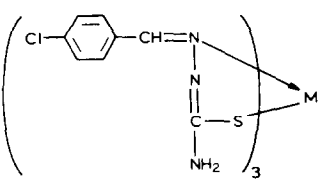
Parameter	Temperature (°C)	
	28	38
Pr(III)–p.Cl.BZH.THSMC		
log k_1	8.40 (7.85)	8.90 (8.90)
log k_2	6.10 (6.00)	6.20 (5.95)
log k_1/k_2	(1.85)	(2.95)
log k_3	4.95 (5.00)	5.00 (5.05)
log β_3	19.45	20.10
$\Delta G°$	−26790	+21418
$\Delta H°$	+21418	+21418
$\Delta S°$		+161
Nd(III)–p.Cl.BZH.THSMC		
log k_1	8.20 (8.10)	8.7 (8.4)
log k_2	5.05 (5.85)	5.8 (6.6)
log k_1/k_2	(2.25)	(1.8)
log k_3	5.00	5.2 (5.2)
log β_3	18.85	19.7
$\Delta G°$	−25964	−28036
$\Delta H°$	+25701	+25701
$\Delta S°$		+173

[a] Units: ΔG^0, cal mol^{-1}; ΔH^0, cal mol^{-1}; ΔS^0, cal mol^{-1} o_C^{-1}. Data in parentheses are from the formation curves of Bjerrum [5].

collisions due to the increased kinetic energy of the participating molecules. The reactions are endothermic in nature ($+\Delta H^0$), supporting these inferences. Negative ΔG^0 values indicated the thermodynamic feasibility of the reactions: this increased with the more negative ΔG^0 values encountered at higher temperatures. Positive ΔS^0 values were favourable for the reactions.

The solution data are given in Table 1.

Based on the present study and on our earlier report on p.Cl.BZH.THSMC [3] we propose the following tentative structure for tris(*p*-chlorobenzaldehydethiosemicarbazonato)M(III), where M = Pr or Nd:



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