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Note

STABILITY AND THERMODYNAMICS OF Gd^{III}- AND Eu^{III}-*p*-CHLOROBENZALDEHYDETHIOSEMICARBAZONE SYSTEMS

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The carcinostatic properties of metal complexes of thiosemicarbazones have greatly interested many researchers, and a tremendous amount of work has been done on the subject. Sawhney and co-workers have made various contributions to this research effort [1–3]. The present communication is concerned with the solution chemistry of Gd^{III}- and Eu^{III}-*p*-chlorobenzaldehydethiosemicarbazone systems. A likely explanation of the stability and thermodynamics of the two systems is proposed.

EXPERIMENTAL

The chemicals used were of analytical grade. The instrumental and experimental conditions were as described in an earlier report [3].

RESULTS AND DISCUSSION

The whole study was performed within a thermodynamically true environment (0.1 M KNO_3, infinite dilution 50% acetone in water). The solution contains titratable H^+, as a consequence of the ligand undergoing tautomerism owing to conjugation in the dominant form. It is therefore possible to study these systems in solution.

The value of $\bar{n}$ for these Gd- and Eu-*p*-chlorobenzaldehydethiosemicarbazone systems is 3, indicating stepwise formation of complex species of stoichiometry 1 : 1, 1 : 2 and 1 : 3. It has been proposed by various researchers that the salt-forming group (SH) and the terminal hydrazine N^{III} atom are possible interaction sites in this process. The trend of stepwise formation constants ($\log k_1 > \log k_2 > \log k_3$) indicates that the bond strength of successive attachment of ligand molecules in solution decreases.

The value of $\log(k_1/k_2)$ was found to be $\geqslant 2.5$ (Table 1), so use of the Bjerrum half-integral technique was clearly justified. A graphical procedure

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TABLE 1

Solution data for Gd^{III}- and Eu^{III}-*p*-chlorobenzaldehydethiosemicarbazone systems

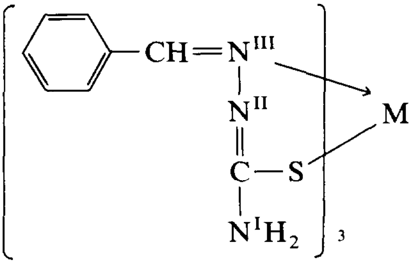
Metal	Parameter [a]	Method [b]	Temperature (° C)	
			28	38
Gd^{III}	$\log k_1$	A	9.50	8.00
		B	9.60	7.90
	$\log k_2$	A	6.65	5.60
		B	6.90	5.90
	$\log(k_1/k_2)$	A	2.85	2.40
	$\log k_3$	A	5.10	5.00
		B	5.30	5.10
	$\log \beta$	A	21.96	19.00
		B	21.80	18.90
	mean		21.88	18.95
	$\Delta G^{\ominus}$		-30.99	-26.97
	$\Delta H^{\ominus}$		-124.23	-124.23
	$\Delta S^{\ominus}$			-310.00
Eu^{III}	$\log k_1$	A	9.65	8.65
		B	9.65	8.85
	$\log k_2$	A	6.45	5.75
		B	6.50	6.10
	$\log k_1/k_2$	A	3.20	2.90
	$\log k_3$	A	5.01	5.00
		B	5.00	5.00
	$\log \beta$	A	21.11	20.30
		B	21.15	19.95
	Mean		21.13	20.13
	$\Delta G^{\ominus}$		-27.73	-28.65
	$\Delta H^{\ominus}$		-42.84	-42.84
	$\Delta S^{\ominus}$			-370.00

[a] ΔG (kcal mol^{-1}), ΔH (kcal mol^{-1}), ΔS (cal mol^{-1} deg^{-1}).

[b] A = Bjerrum technique, B = graphical method.

was also used to determine the stability constants for the systems. Thermodynamic parameters were determined from the means of the values obtained by these two methods.

The stepwise formation constants (k_1, k_2, k_3) were lower at the higher temperature. This suggests that the metal *p*-chlorobenzaldehydethiosemicarbazone reaction is favoured by low temperatures, owing to the decreased kinetic energy of (and hence decreased number of collisions between) molecules involved in the reaction, which would lower the stability of the system. These inferences are supported by the values obtained for $-\Delta H^{\ominus}$ which also hint at the probable presence of covalency in the resulting complexes in solution. Solvent effects brought about negative values of $\Delta S^{\ominus}$. The negative $\Delta G^{\ominus}$ values obtained suggest that the reactions occur spontaneously, the Eu–ligand reaction becoming feasible only as the value of $\Delta G^{\ominus}$ becomes more negative at higher temperatures. On the basis of the results of the present study, and findings from earlier works, the following structure can be proposed.



M ≡ GD or Eu

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