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Note

STABILITY AND THERMODYNAMICS OF Cu(II)-, Co(II)-, Ni(II)-, Zn(II)- AND Mn(II)-*p*-CHLOROBENZALDEHYDETHIOSEMICARBAZONE SYSTEMS

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In continuation of previous communications dealing with the solution chemistry of metal-substituted thiosemicarbazone systems [1-4], an attempt to investigate the Cu(II)-, Co(II)-, Ni(II)-, Zn(II)- and Mn(II)-*p*-chlorobenzaldehydethiosemicarbazone (abbreviated to *p*-Cl.BzH.THSMC) systems in 50% (v/v) acetone/water at an ionic strength $I = 0.1$ M (KNO_3) has been made; their stability and thermodynamics are also discussed.

EXPERIMENTAL

Chemicals used were of AnalaR grade. Equimolar solutions of *p*-chlorobenzaldehyde (in acetone) and aqueous thiosemicarbazide were mixed; vigorous shaking of the mixture gave a yellow coloured precipitate which was recrystallised in acetone prior to use. Chemical analysis data tallied with the accompanying formula ($C_8H_8N_3SCl$). Found: C, 43.30; H, 3.90; N, 19.10; S, 15.50; Cl, 17.46%. Calcd: C, 44.96; H, 3.75; N, 19.67; S, 14.99; Cl, 16.63%.

The procedure and conditions applied have been reported earlier [3].

RESULTS AND DISCUSSION

Like *p*-nitrobenzaldehydethiosemicarbazone, *p*-chlorobenzaldehydethiosemicarbazone tautomerises in solution with the dominating thiol form possessing conjugation (=N-N=C-) that has been considered in the subsequent interpretation of the systems at hand.

The system was carried out near infinite dilution and at constant ionic strength (0.1 M KNO_3) ensuring that all the activity coefficients of the chemical species involved are equal to unity and hence the calculation of the thermodynamic formation constants is possible [5].

Formation functions, ${}^{P}K^{H}$, $\bar{n}_H$, $\bar{n}$ and pL were calculated using the Irving-Rossotti [6] and Bjerrum expressions [7].

Plots of $\bar{n}$ vs. pL of the systems were complete at both ends. Log k_1/k_2 values stood at $\geqslant 2.5$, justifying the consideration of Bjerrum's method for the constants' values. Other methods for calculation were the pointwise and graphical methods, and that due to Bjerrums' equation [7].

Table 1 incorporates the mean values of log ${}^{P}K^{H}$, log k_1 and log k_2.

In all the metal ligand systems, $\bar{n}$ neared 2, indicating the existence of stoichiometries of 1 : 1 and 1 : 2 of complex species in solution.

To prevent metal hydrolysis, each set comprised 5 : 1 *p*-Cl.BzH.THSMC/metal. During pH-metric titration, the metal-*p*-Cl.BzH.THSMC curve separated from the *p*-Cl.BzH.THSMC curve under experimental conditions, constituting evidence in favour of the –SH group in solution and the participation of the anion of *p*-Cl.BzH.THSMC.

On analysing the constants' values, it is seen that the attachment of the first molecule of *p*-Cl.BzH.THSMC to either metal is stronger than the second one (log $k_1 >$ log k_2). Further, with increase in temperature the log ${}^{P}K^{H}$, log k_1 and log k_2 values decrease indicating low temperature to be favourable for complexation because of the decrease in kinetic energy of molecules participating in the reaction, suggesting lowering of the stability of the system as temperature rises. Negative ΔG° values suggest that the reactions are spontaneous in nature; with the assumption that less negative values of ΔG° lower the feasibility of the reaction. All the reactions are enthalpy controlled; the higher values of $-\Delta H^{\circ}$ for all the systems suggest

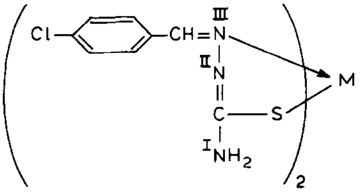
TABLE 1

Stability constants and thermodynamic functions of metal complexes of *p*-chlorobenzaldehydethiosemicarbazone

Metal ion	Metal–ligand stability	Temp. (°C)		ΔG (kcal mol^{-1})		ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} °C^{-1})
		28	38	28	38		
	log ${}^{P}K^{H}$	10.25	9.70				
Cu(II)	log k_1	8.85	8.05				
	log k_2	6.40	5.50				
	log β_2	15.25	13.55	−21.00	−19.28	−73.68	−174.92
Ni(II)	log k_1	8.60	8.19				
	log k_2	6.29	5.19				
	log β_2	14.89	13.38	−20.51	−19.04	−62.96	−141.22
Co(II)	log k_1	9.11	8.30				
	log k_2	5.86	5.65				
	log β_2	14.97	13.95	−20.62	−19.85	−32.96	−42.15
Zn(II)	log k_1	8.95	8.14				
	log k_2	6.57	5.09				
	log β_2	15.52	13.23	−21.38	−18.83	−109.23	−290.68
Mn(II)	log k_1	8.89	8.13				
	log k_2	6.98	5.76				
	log β_2	15.87	13.89	−21.86	−19.77	−89.53	−224.31

the presence of a considerable degree of covalency in the metal complexes, probably through the terminal hydrazine nitrogen (N^{III}) atom, concluded through spectral studies by Malic and Phillips [8], Haines and Sun [9] Beecroft et al. [10] and Calzolari et al. [11]. Complexation between Cu(II), Co(II), Ni(II), Zn(II) or Mn(II) and *p*-Cl.BzH.THSMC are exothermal reactions (Table 1) which corroborates the earlier inferences that low temperature is favourable for complexation.

Pooling earlier considerations on the systems the following structure of the metal–*p*-Cl.BzH.THSMC complexes is suggested.



Bis(*p*-chlorobenzaldehydethiosemicarbazonato)M(II) (where M = Cu(II), Co(II), Ni(II), Mn(II) and Zn(II)).

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