Thermochimica Acta, 116 (1987) 373–376
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

STABILITY AND THERMODYNAMICS OF BINARY COMPLEXES OF DIVALENT METAL IONS WITH *p*-NITROBENZALDEHYDESEMICARBAZONE

S.S. SAWHNEY, K. URMILA SALUJA and M.M. SINGH
Chemistry Department, DAV (P.G.) College, Dehra Dun 248 001 (India)
(Received 1 December 1986)

Sawhney et al. have previously studied systems consisting of metals and *p*-nitrobenzaldehydethiosemicarbazone [1,2]. This study on the interaction of some bivalent metals: Cu, Ni, Co, Mn and Zn and *p*-nitrobenzaldehydesemicarbazone (hereinafter abbreviated as *p*.N.BzH.SMC) has been carried out under thermodynamic conditions.

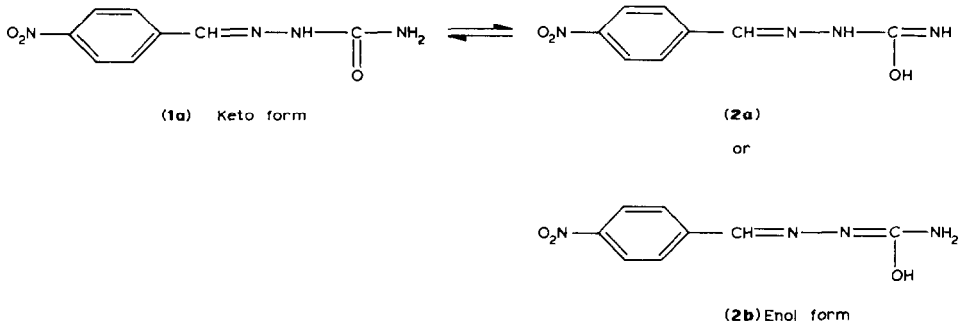
EXPERIMENTAL

All the chemicals used were of analytical grade. Equimolecular quantities of *p*.N.BzH.SMC in ethanol and semicarbazide hydrochloride solution in water were mixed and shaken vigorously to obtain fine crystals of *p*.N.BzH.SMC. Found: C, 47.05; H, 3.69; N, 26.80%. Calc: C, 46.15; H, 3.85; N, 26.92%. The sets used: (a) 4×10^{-3} M HCl, 10^{-1} M KCl; (b) 4×10^{-3} M HCl, 10^{-1} M KCl, 10^{-3} M *p*.N.BzH.SMC; (c) 4×10^{-3} M HCl, 10^{-1} M KCl, 10^{-3} M *p*.N.BzH.SMC, 2×10^{-5} M metal, were pH-metrically titrated with 0.1 M NaOH. The shapes of the curves (pH vs. base), after applying correction to the pH value (for volume and nonaqueous media according to Van Uitert and Haas [3]), were as usual.

RESULTS AND DISCUSSION

p.N.BzH.SMC like *p*-nitrobenzaldehydethiosemicarbazone, displaying tautomerism, assumes acidic nature, attributable to the dominating form with conjugation (=N–N=) (Scheme 1). With the aid of the Irving and Rossotti expression [4], the determination of the protonation constant of *p*.N.BzH.SMC was attempted. It was found that log ${}^{P}K^{H} = 10.55$ (28°C) and 9.60 (38°C). The metal hydrolysis was checked by keeping a 5:1 (ligand:metal) ratio in each set. Plots of n and pL calculated according to

0040-6031/87/$03.50



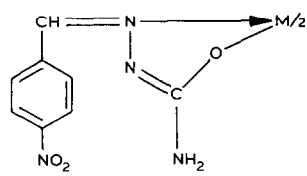
Scheme 1.

Bjerrum [5] could not provide data adhering to Bjerrum conditions ($\log k_1/k_2 \geqslant 2.5$); other methods, viz. least squares, pointwise calculation and graphical methods were depended on to ensure data reliability (Table 1).

The whole study at infinite dilution and at constant ionic strength was demonstrative of thermodynamically true solution data [6]. The reaction of *p*.N.BzH.SMC and metals in the reference was low temperature dependent as indicated by the decrease in the value of the constants with a rise in temperature because of the decrease in the number of collisions with a decrease in kinetic energy of the molecules involved in the reactions. Negative ΔG^0 values made the reactions feasible, and their feasibility decreased at higher temperature as these values became less negative under the experimental conditions. The reactions are exothermic in nature supporting earlier drawn inferences, and are also enthalpy controlled. The ΔH^0 values indicated the presence of considerable covalency in the metal complexes in solution.

The above inferences are contrary to earlier expressed opinions on the systems involving these metals and *p*-nitrobenzaldehydethiosemicarbazone [1].

pH studies hinting that n approached 2 and limiting conditions being reached with 1 : 3 (metal:ligand) in all the systems, led us to believe the existence of complex species with 1 : 1 and 1 : 2 stoichiometries.



Scheme 2. Bis(*p*-nitrobenzaldehydesemicarbazonato) M^{2+} (M = Cu(II), Ni(II), Co(II), Mn(II) and Zn(II)).

TABLE 1

Stability and thermodynamics of metal–*p*.N.BzH.SMC systems

Metal		28 °C	38 °C
Cu	Log k_1	9.90	7.97
	Log k_2	6.19	5.58
	Log k_1k_2	16.09	13.55
		(16.90)	(18.33)
	ΔG^0	−22.16	−19.28
	ΔH^0		−108.80
	ΔS^0		−287.85
Ni	Log k_1	9.73	8.55
	Log k_2	6.87	4.48
	Log k_1k_2	16.60	13.39
		(20.52)	(14.10)
	ΔG^0	−22.86	−19.08
	ΔH^0		−137.50
	ΔS^0		−380.84
Co	Log k_1	9.73	9.23
	Log k_2	6.63	5.39
	Log k_1k_2	16.36	14.62
		(18.29)	(14.65)
	ΔG^0	−22.56	20.81
	ΔH^0		−75.39
	ΔS^0		−175.49
Mn	Log k_1	10.55	8.85
	Log k_2	7.56	5.77
	Log k_1k_2	18.22	14.62
		(17.97)	(15.51)
	ΔG^0	−24.72	−20.81
	ΔH^0		−142.65
	ΔS^0		−391.76
Zn	Log k_1	10.26	8.83
	Log k_2	7.86	5.58
	Log k_1k_2	18.12	14.41
		(18.94)	(18.27)
	ΔG^0	−24.96	−20.51
	ΔH^0		−158.92
	ΔS^0		−445.05

The stability order of the systems does not follow either the Irving–Williams rule [7] or any of the empirical orders reviewed by Irving and Williams and Mellor and Melay [8].

An earlier report on the systems studied after replacing *p*.N.BzH.SMC by *p*.N.BzH.THSMC (*p*-nitrobenzaldehydethiosemicarbazone) by Sawhney et al. [1] referred to the better systems' stability than the ones in the reference;

an explanation to this effect has been sought considering the electronegativity values of S (2.3) and O (3.5) on the Pauling scale. S is a less effective participant in hydrogen bonding than O in the ligands. The considerably less polar nature of S–H (in *p*.N.BzH.THSMC) in comparison to *p*.N.BzH.SMC which has an O–H bond appears to render a weak hydrogen bonding in solution making proton and metal complexes of *p*.N.BzH.SMC comparatively less stable. This study together with the available data [9–12] on the systems may afford the situation indicated in Scheme 2 in the metal complexes.

REFERENCES

1 S.S. Sawhney and R.M. Sati, Thermochim. Acta, 61 (1983) 365.
2 S.S. Sawhney and S.K. Chandel, Thermochim. Acta, 71 (1983) 209.
3 L.G. Van Uitert and C. Haas, J. Am. Chem. Soc., 75 (1953) 451.
4 H. Irving and H. Rossotti, J. Chem. Soc., (1953) 3397; (1954) 2904.
5 J. Bjerrum (Ed.), Metal Ammine Formation in Aqueous Solution, Haase, Copenhagen, 1941, p. 298.
6 H.M. Irving and R.J.P. Williams, Nature (London), 162 (1948) 746; J. Chem. Soc., 3192 (1953).
7 D.P. Mellor and L.E. Maley, Nature (London), 159 (1947) 394; 161 (1948) 436.
8 A. Goronback and S.E. Rasmussen, Acta Chem. Scand., 16 (1962) 2325.
9 M. Akhtar Malic and J. David Phillips, Aust. J. Chem., 28 (1975) 305.
10 A. Ronaldhaines and K.W.K. Sun, Can. J. Chem., 20 (1968) 3241.
11 B. Beecroft, M.J.M. Campbell and R. Grzeskowiak, J. Inorg. Nucl. Chem., 36 (1974) 55.
12 C.B. Mahto, J. Indian Chem. Soc., 57 (1980) 553.