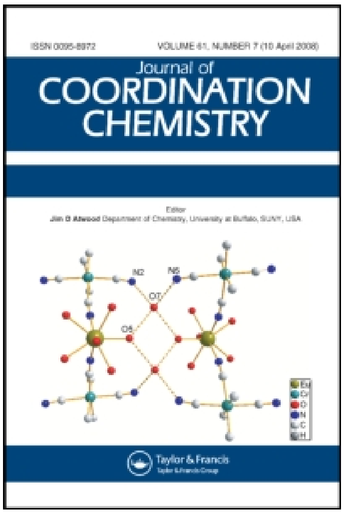

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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First published on: 01 April 2010

To cite this Article Mahajan, Rakesh K. , Vohra, Kulwinder K. , Arora, Poonam , Sharma, Rekha and Lobana, T. S.(2010) 'Determination of stability constants and thermodynamic parameters for interaction of thiosemicarbazones with divalent metal ions', Journal of Coordination Chemistry, 63: 7, 1220 — 1227, First published on: 01 April 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958971003735457

URL: http://dx.doi.org/10.1080/00958971003735457

Journal of Coordination Chemistry
Vol. 63, No. 7, 10 April 2010, 1220–1227

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Determination of stability constants and thermodynamic parameters for interaction of thiosemicarbazones with divalent metal ions

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(*Received 18 May 2009; in final form 18 November 2009*)

The Calvin–Bjerrum pH titration technique as modified by Irving and Rossotti has been applied to determine the stability constants of complexes of a series of thioligands, namely benzaldehyde thiosemicarbazone, pyridine-2-carbaldehyde thiosemicarbazone, and cyclopentanone thiosemicarbazone with divalent metal ions (Cu, Cd, Co, Ni, Pb, and Zn). The studies were carried out in 50% v/v dioxane-water at different temperatures (293 K, 303 K, and 313 K) keeping ionic strength at 0.1 mol KNO_3. The thioligands undergo deprotonation of only one proton (–N^2H–) of a thiosemicarbazone [$R^1R^2C^2{=}N^3{-}N^2(H){-}C^1({=}S)N^1H_2$]. Thermodynamic parameters, such as free energy, enthalpy, and entropy have also been evaluated. The investigations represent the first report of the solution phase studies in metal–thiosemicarbazone chemistry.

Keywords: Thiosemicarbazone; Calvin–Bjerrum technique; Stability constant; Thermodynamic parameters

1. Introduction

Metal chelates occur commonly in biological fluids, as millions of potential ligands compete for metal ions found *in vivo* [1, 2]. Hence, metal complexes are a focus of biochemistry, with a study of their structures, stabilities, and reaction mechanisms. The nature of metal ion, the nature of ligand, the dielectric constant, the ionic strength, and the temperature affect the stability constants [3–7]. Most knowledge about metal complexes originates from thermodynamic studies. Stability constants give the degree of metal ion interaction with a ligand, valuable information about the mechanism, and possible structure correlation between a metal ion and the structure of a ligand. Thiosemicarbazones and their complexes with transition metal ions find applications in various fields of chemistry and life sciences with a wide range of physiological activities,

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958971003735457

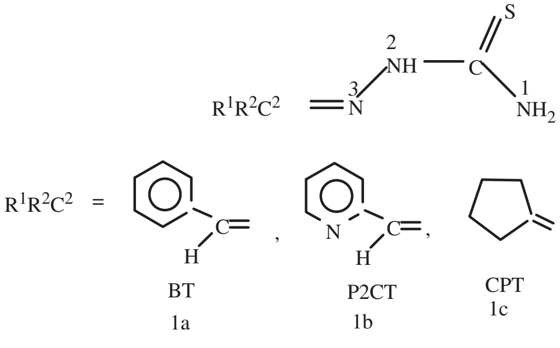
analytical applications, and antioxidant and biological properties, such as antiviral, antitubercular, antimalarial, and antifungal properties [8–14].

Thiosemicarbazones (N, S- donor ligands) (scheme 1) with variable bonding properties lead to compounds, which differ in their nuclearities [15–20]. Solid state studies have been reported [21–32], but there is no report on the stability constants and the thermodynamic properties of complexes in solution. Given the role of metal chelators in the biological systems, the interaction of thioligands (scheme 1) with divalent metals in the solution phase is important. This article deals with the determination of the stability constants and the thermodynamic parameters of complexes of Cu(II), Cd(II), Co(II), Ni(II), Pb(II), and Zn(II) with benzaldehyde thiosemicarbazone (BT), pyridine-2-carbaldehyde thiosemicarbazone (P2CT), and cyclopentanone thiosemicarbazone (CPT). The method of Irving and Rossotti [33] has been employed to determine $\log K$ values for the determination of stability constants.

2. Experimental

2.1. *Materials*

All chemicals were of A.R. grade. 1,4-Dioxane and EDTA were obtained from Fluka and metal nitrates were obtained from Aldrich and used without purification. The ligands BT (1a), P2CT (1b) and CPT (1c) were synthesized by methods described in the literature [34–37]. 1,4-Dioxane was purified by standard procedure [36]. The ligand solutions were prepared in 1,4-dioxane. All the metal ion solutions were prepared by dissolving their nitrates in doubly distilled deionized water and standardized by standard volumetric methods. A solution of KNO_3 (0.1 mol) was used to maintain the appropriate ionic strength. The pH measurements were performed on an Elico pH meter model LI 120 using a calomel electrode assembly in 50% v/v dioxane-water at 20°C, 30°C, and 40°C, and at ionic strength of 0.1 mol. The pH meter was calibrated with suitable buffers before use.



Scheme 1. Structures of thiosemicarbazone ligands.

2.2. *Methods*

The three solutions (total volume 50 mL in each case) were prepared as follows: (A) 2.5 mL of 1.0×10^{-2} mol HNO_3, (B) 2.5 mL of 1.0×10^{-2} mol $HNO_3 + 5.0$ mL of 2.5×10^{-2} mol ligand, (C) 2.5 mL of 1.0×10^{-2} mol $HNO_3 + 5.0$ mL of 2.5×10^{-2} mol ligand + 2.5 mL of 1.0×10^{-2} mol metal ion solutions. A calculated amount of 1.0 mol KNO_3 solution was added to maintain the desired ionic strength (0.1 M). The solutions labeled A, B, and C were titrated against KOH (0.005 M) prepared in 50% v/v dioxane-water. The curves were obtained from plots of pH *versus* volume of alkali (KOH) added. The slopes of the curves are shown in figure 1.

3. Results and discussion

Figure 1 represents the acid titration curve, the ligand titration curve (for P2CT), and the metal ion titration curves for Cu(II), Cd(II), Co(II), Ni(II), Pb(II), and Zn(II) at 303 K. Similar plots have also been obtained at three different temperatures (293, 303, and 313 K) as well as for BT and CPT. Nitrate has no influence on the stability constants. A sharp increase in pH from 4 to 10.5 represents inflection point that corresponds to the neutralization of one proton [38].

The proton–ligand stability constant and the values of $\overline{n}_A$ (the degree of formation of the proton complex) were calculated at different pH values using equation (1):

$$\overline{n}_A = Y + \frac{(V' - V'')}{(V^\circ - V')}\frac{(N + E^\circ)}{T_L^\circ}, \tag{1}$$

where Y = number of replaceable hydrogen ions, V° = total volume (50 mL), V' = volume of alkali used by acid, V'' = volume of alkali used by acid and ligand, N = concentration of alkali, E° = total strength of acid, and T_L° = total concentration of ligand.

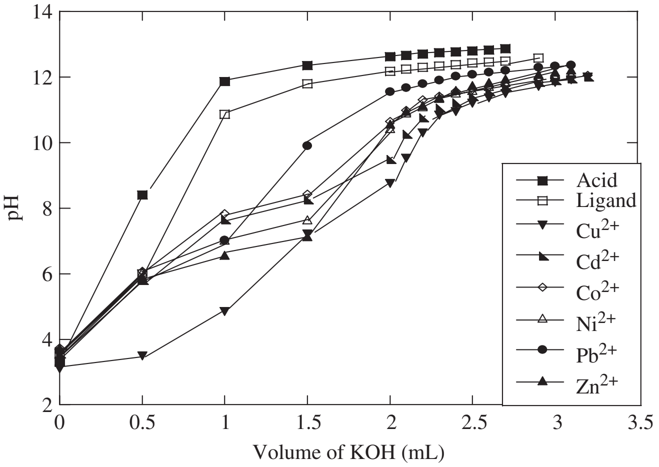


Figure 1. Potentiometric titration curve of P2CT at 303 K and 0.1 mol KNO_3.

The proton–ligand (P2CT) formation curve was obtained by plotting the degree of formation ($\overline{n}_A$) of the proton complex against pH (figure 2). The values of log K_1^{H} were obtained from curves corresponding to $\overline{n}_A$ of 0.5. The extension of curves over a range of $\overline{n}_A$ (0 to 1) provided log K_1^{H} for the thiosemicarbazone derivative (P2CT). The value of log K_1^{H} indicated the monobasic nature of the ligand with one dissociable proton present in each thiosemicarbazone. High temperature favors the deprotonation of the ligand which in turn favors the formation of a stable metal–ligand complex for BT. The reverse is true for the complexation of CPT and the optimum temperature of complexation for P2CT is 303 K. A decrease or increase in temperature from 303 K leads to a decrease in the stability for the complexes of P2CT. The value of $\overline{n}$ (average number of ligands attached per metal ion) was calculated using equation (2):

$$\overline{n} = \frac{(V''' - V'')}{(V^{\circ} - V'')} \frac{(N + E^{\circ})}{\overline{n_A} T_{\mathrm{M}}^{\circ}}, \tag{2}$$

where V''' = volume of KOH used for acid (HNO_3), ligand and metal ion, T_{M}° = total concentration of the metal ion and other parameters are as given in equation (1). The $\overline{n}$ values show the formation of 1 : 1 metal–ligand complex.

The free ligand exponent, pL was calculated using equation (3):

$$pL = \log\left[\frac{\sum \beta_n^H \left(\frac{1}{anti \log B}\right)}{T_{\mathrm{L}}^{\circ} - \overline{n} T_{\mathrm{M}}^{\circ}}\right] \frac{V^{\circ} + V'''}{V^{\circ}}, \tag{3}$$

where β_n^H = proton–ligand stability constant and B is the pH reading corresponding to volume (V'''); the other symbols are same as in equations (1) and (2). Figure 3 is a plot of $\overline{n}$ *versus* pL which represents metal–ligand formation for M^{2+}-P2CT at 303 K. Similar plots were obtained for the other ligands at three different temperatures.

Lack of general behavior of these metal ions towards thiosemicarbazones makes the formation of a polymeric complex negligible [21]. The value of $\overline{n}$ obtained for the metal–ligand system indicates stepwise formation, with probable complexation equilibria:

$$\mathrm{HL} + \mathrm{M}^{2+} \overset{\log \mathrm{k}_1}{\rightleftharpoons} \mathrm{ML} + \mathrm{H}^+$$

$$\mathrm{HL} + \mathrm{ML} \overset{\log \mathrm{k}_2}{\rightleftharpoons} \mathrm{ML}_2 + \mathrm{H}^+.$$

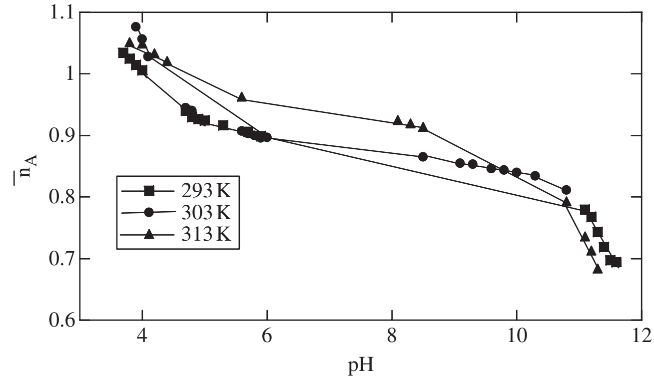


Figure 2. Proton–ligand formation curves at 293, 303, and 313 K for P2CT.

Bjerrum's [39] half integral, interpolation at various $\bar{n}$ values and graphical methods extended to dioxane-water mixture by Van Uitert and Hass [7] were used to calculate $\log K_1$ and $\log K_2$. The values of log β (calculated from $\log K_1$ and $\log K_2$) at three different temperatures are summarized in table 1. The average value of log β has also been determined for the order of stability of a metal–ligand complex. The stability constants vary in the order:

For CPT Cu(II) > Zn(II) > Ni(II) > Pb(II) > Cd (II) > Co(II)
For P2CT Cu(II) > Ni(II) > Zn(II) > Pb(II) > Cd (II) > Co(II)
For BT Cu(II) > Zn(II) > Co(II) > Ni(II) > Cd (II) > Pb(II)

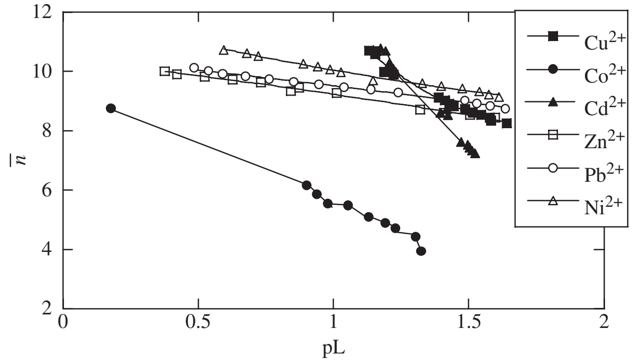


Figure 3. Metal–ligand formation curves at 303 K for P2CT.

Table 1. Protonation constants of various ligands and metal–ligand stability constants of complexes at three different temperatures.

		Stability constant log β		
Ligand	Metal ion	293 K	303 K	313 K
BT	H^+	8.5	8.45	8.6
	Cu^{2+}	15.14	14.6	15.3
	Cd^{2+}	10.30	10.40	11.30
	Co^{2+}	12.72	13.30	13.60
	Ni^{2+}	11.43	12.00	13.40
	Pb^{2+}	7.90	11.70	12.20
	Zn^{2+}	13.56	14.10	13.20
P2CT	H^+	11.92	11.96	11.62
	Cu^{2+}	21.06	21.56	20.06
	Cd^{2+}	12.20	10.75	15.25
	Co^{2+}	14.30	14.05	9.35
	Ni^{2+}	19.00	19.60	18.55
	Pb^{2+}	15.30	19.15	14.85
	Zn^{2+}	18.50	18.30	15.50
CPT	H^+	11.93	11.96	11.76
	Cu^{2+}	22.08	21.96	21.57
	Cd^{2+}	14.15	13.75	13.05
	Co^{2+}	13.85	13.20	13.00
	Ni^{2+}	15.85	15.10	14.60
	Pb^{2+}	15.55	13.45	14.80
	Zn^{2+}	16.35	16.20	15.60

due to the characteristic features of the substituents of the thiosemicarbazones. Among the metal ions under investigation, Cu(II) ion has the lowest value of ionic radius (0.69 Å) and hence forms the most stable complexes with all the ligands. For Cu(II)-thioligand complexes, the stability constants follow the order CPT > P2CT > BT. The stability constants of metal-BT complexes increase with the increase in temperature, whereas for metal–CPT complexes the stability constants decrease with the increase in temperature (table 1). This is attributed to phenyl substituent at C^2 of BT and keto group in CPT which appears to control the stability. Finally, P2CT has a pyridyl substituent at C^2 which affects complexation, as stability constants first increase, then decrease with increase in temperature; 303 K is optimum for the complexation of metal–P2CT complexes.

Overall changes in the free energy of formation (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) accompanying complexation have also been determined by using temperature coefficient and the Gibbs Helmholtz equation (table 2). The free energies of formation (ΔG°) are negative showing spontaneous complex formation. The free energy change is negative in all cases. ΔH° favors the greater complexation of Cu(II) with various ligands. The complexation of CPT with different metal ions is endothermic but the Gibbs free energy is negative, which indicates that for CPT entropy favors complexation. For other ligands, either the exothermic nature or the increase in entropy favors complex formation. The change in enthalpy and the change in entropy nicely compensate each other to make the overall free energy change negative.

Table 2. Thermodynamic parameters of various metal–ligand complexes.

		$-\Delta G$ (kJ mol^{-1})			$-\Delta H$ (kJ mol^{-1})	ΔS (J mol^{-1} deg^{-1})
Ligand	Metal ion	293 K	303 K	313 K	303 K	303 K
BT	H^+	47.69	49.02	51.54	−9.36	13242.0
	Cu^{2+}	84.90	84.60	91.70	−17.77	220.49
	Cd^{2+}	57.80	60.60	67.70	−89.97	97.06
	Co^{2+}	71.40	73.80	81.50	−76.30	0.0082
	Ni^{2+}	64.10	69.60	80.30	−175.55	349.63
	Pb^{2+}	44.30	67.80	73.10	−367.6	989.47
	Zn^{2+}	76.10	81.80	79.10	35.85	−388.18
P2CT	H^+	66.87	69.39	69.64	−27.47	3228.67
	Cu^{2+}	118.1	125.0	120.22	−93.69	722.03
	Cd^{2+}	68.44	62.37	91.39	285.34	−735.87
	Co^{2+}	80.22	81.51	56.04	639.22	−1840.63
	Ni^{2+}	106.5	113.7	111.17	−44.34	519.84
	Pb^{2+}	85.83	111.1	98.00	−63.20	575.25
	Zn^{2+}	103.7	106.6	93.19	49.7	−187.08
CPT	H^+	66.93	69.39	70.48	−15.61	2833.33
	Cu^{2+}	123.8	127.4	129.27	−66.58	640.20
	Cd^{2+}	79.38	79.77	78.21	−97.55	640.20
	Co^{2+}	77.70	76.58	77.90	−37.41	376.21
	Ni^{2+}	88.92	87.60	87.50	−109.14	649.31
	Pb^{2+}	87.24	78.03	88.70	−55.91	442.05
	Zn^{2+}	91.73	93.99	93.49	−181.97	910.76

4. Conclusions

Metal–ligand stability constants have been determined using potentiometric techniques. The Calvin–Bjerrum pH titration technique modified by Irving and Rossotti has been applied to determine the stability constants of BT, P2CT, and CPT with Cu(II), Cd(II), Co(II), Ni(II), Pb(II), and Zn(II). The potentiometric studies on these ligand–divalent metal ion systems give an order for stability constants closely resembling the Irving–William series. This order is attributed to the presence of varying substituents at C^2 of the thioligands. Complex formation is spontaneous in the solution phase.

Acknowledgment

The authors are grateful to CSIR for financial support.

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