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Studies on Mangenese (II), Cobalt(II), Nickel(II), Copper(II) and Zn(II) complexes of substituted phenyl-thiazolyl-thiosemicarbazide

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ABSTRACT

Thiazolyl thiosemicarbazide consists of a thiazole moiety in the structure. The compounds belonging to the thiazole ring systems have shown considerable activity in various fields including medicinal chemistry. Vitamin B1, sulphatiazole, promizole, nitridazole, aminitrazole, and thiabendazole, all contain thiazole ring in one form or other. Thiosemicarbazide containing –NCS group are known to possess pronounced biological activities. Thiosemicarbazide along with thiosemicarbazones have been used in various life saving drugs and drug action of these compounds was found to have been increased when administered in the form of their metal complexes. However a survey of literature reveals that no work has been done with substituted thiazolyl thiosemicarbazides. In the present work we investigate the complex formation process between some substituted thiazolyl thiosemicarbazides synthesised in our laboratory for the first time and various metal ions belonging to transition and inner transition series. The stability of different complexes follows the order: Mn < Co < Ni < Cu > Zn.

Keywords : Thiazolyl Thiosemicarbazide, Metal Ions, Metal-Ligand Complexes, Stability, Thermodynamics

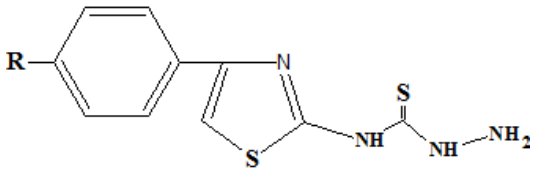
I. INTRODUCTION

Thiosemicarbazides are known to possess antiviral[1], fungicidal[2], and antitubercular[3] activities. They are known to act as inhibitors in the corrosion of Aluminium and Zinc[4]. The metal complexes of thiosemicarbazides have been known for pharmacological applications.[5] Crim *et al*[6] have shown the importance of metal chealets against cancer. They have been used in various life saving drugs.[7,8] The drug action of these compounds was found to have been increased when administered in the form of their metal complexes.[9,10]

It was therefore decided to investigate the complex formation process between certain metal ions, commonly occurring in the physiological systems and various substituted thiosemicarbazides and to see the effect of substituents (if any) in the organic compound part of the complexes. The investigation was carried out by using Calvin-Bjerrum potentiometric titration technique. (Ionic strength 0.1M, 30^0 C, Medium – dioxane)

II. EXPERIMENTAL

All the chemicals used were of Analytical grade. The metal ions were used in the form of their nitrates and were estimated by EDTA titrations.[11] Dioxane was purified by standard method.[12] The thiosemicarbazides N-[4'-phenylthiazole-2'-yl]thiosemicarbazide(1), N-[4'-(4"-Bromophenyl)thiozole-2'-yl]- thiosemicarbazides (2), N-[4'- (4"-chlorophenyl)thiozole-2'-yl]-thiosemicarbazides (3), N-[4'-(4"-methylphenyl)thiozole-2'-yl]- thiosemicarbazides (4), and N-[4'-(4"-Aceta-amido) thiozole-2'-yl]-thiosemicarbazide were prepared and purified by the methods described earlier.[13]



1; R = -H
2; = -Br
3; = -Cl
4; = $-CH_3$

5; = 

Scheme 1. The basic structure of ligand

The Calvin-Bjerrum titration technique involving the titration of i) 4 X 10^{-3} M $HClO_4$(A); (ii) 4 X 10^{-3} M $HClO_4$ (A)+ 2 X 10^{-3} M ligand (A+L) and (iii) 4 X 10^{-3} M $HClO_4$ + 2 X 10^{-3} M ligand (A+L+M) + 4 X 10^{-4} M metal ion solution against standard (1.833 X 10^{-1} N) carbonate free NaOH solution. An approximate quantity of 1M $NaClO_4$ solution was added to each of the above mixtures to maintain constant ionic strength of 0.1M. The total volume of each of the mixture was made upto 50 ml so that the solution were 50% (v/v) with respect to dioxane. A Elico LI-120 pH meter having an accuracy of ± 0.01 pH unit with combined electrodes,was used to record the pH values. All the measurements were carried out at 30 ± 0.1° C

Calculations of $\overline{nA}$ pk, n, PL and logK were done by point wise method of Irving-Rossotti.

III. RESULTS AND DISCUSSION

A representative graph of A+L (acid +ligand) and A+L+M (acid+ligand+metal) is shown in Fig.1 Since the pK and log K values obtained were practical values, correction factor of Van Uitert and Fernelius[14] was obtained to get the thermodynamic values. The curve of A + L lies above the acid curve (A) this may be due to association process in the ligands in acidic medium. The same type of behaviour was observed for 2-amino-4-(p-methoxy phenyl ethyl)-thiazole[15]. The values of $\bar{n}$ A indicate that though the ligand has 4 basic nitrogen atoms only one proton is taken up by it like phenanthroline and imidazole.[16,17] This was also observed by Banerjee and Basak[18] in their work with unsubstituted 2-amino-thiazole.

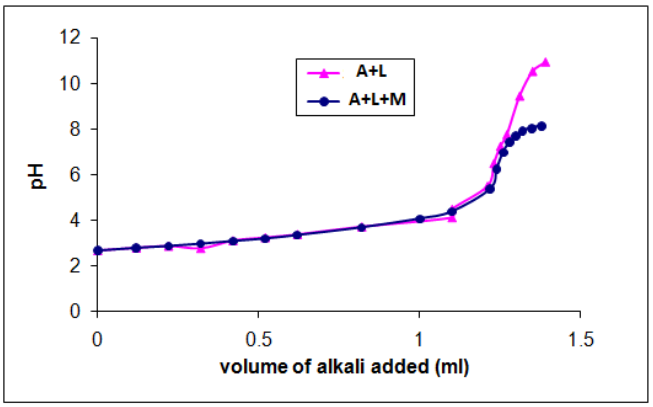


Figure 1. Graph of pH *vs* volume of alkali added

The pH, $\bar{n}$ and PL and log K values for Mn(II) –ligand II system are represented in Table 1.

Table 1. The pH, $\bar{n}$ and PL and log K values for Mn(II) –ligand II

pH	$\bar{n}$	PL	LogK
7.7	0.2272	2.7309	2.1991
8.0	0.2998	2.7377	2.3692
8.2	0.3544	2.7429	2.4825
8.5	0.4815	2.7552	2.7228
8.74	0.7267	2.7797	3.2042

Only the logK values of the metal-ligand complexes could be determined. The $\bar{n}$ values for $logK_2$ were haphazard and in the region of hydrolysis. The stability constants of the meta-ligand complexes are presented in Table 2.

Table 2. Proton-ligand and metal-ligand stability constants of transition metal-thiosemicarbazide complexes in 50% (v/v) aqueous dioxane. Temp -30° C μ = 0.1 M $NaClO_4$

Metal ions	Ligand (I)		Ligand (II)		Ligand (III)		Ligand (IV)		Ligand (V)	
	Log K_1	Log K_2	Log K_1	Log K_2	Log K_1	Log K_2	Log K_1	Log K_2	Log K_1	Log K_2

H+	3.87	-	3.33	-	3.54	-	3.96	-	3.62	-
Mn^{II}	2.546	-	2.60	-	2.72	-	2.64	-	2.66	-
Co^{II}	2.666	-	2.64	-	2.73	-	2.756	-	2.685	-
Ni^{II}	2.706	-	2.69	-	2.75	-	2.777	-	2.76	-
Cu^{II}	2.789	-	2.74	-	2.77	-	2.798	-	2.78	-
Zn^{II}	2.79	-	2.77	-	2.76	-	2.69	-	2.70	-

The stability of the different complexes investigated follow the order, Mn < Co < Ni < Cu > Zn which is in accordance with the Irving and Williams.[19,20] The linear relationship between logK and pK values suggest identical binding sites in all the ligands. The stabilities of Mn(II), Co(II),Ni(II) and Cu(II) complexes were higher than Zn(II) complexes. To confirm the possible correlation, $\log K_1$ values of Co(II) complexes of present series ligands were plotted against $\log K_1$ values of Ni(II) complexes of corresponding ligands (Fig. 2)

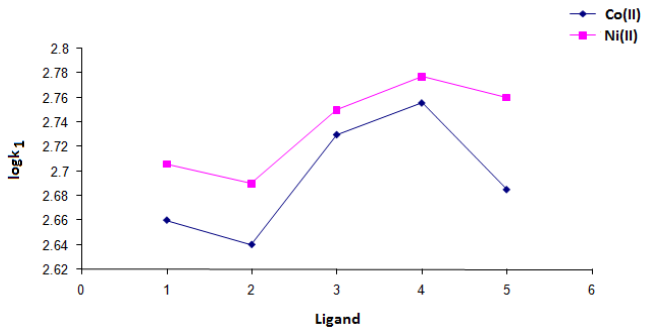


Figure 2. Plot of $\log K_1$ values of Co(II) and Ni(II) complexes of corresponding ligands.

The $\log K_1$ values of Mn(II) complexes were slightly less than those of Co(II), Ni(II), Cu(II) and Zn(II). This was probably due to the bigger size of the thiosemicarbazide molecule which caused steric hindrance in the complex formation.

For determining the Thermodynamic parameters ΔG, ΔS and ΔT, the dissociation constants were determined using the quick titration method developed by Mali and Pethe[21] which utilizes the half neutrilizaion principle. The corresponding values are reported here. The practical proton ligand stability constants of various ligands at different temperatures are represented in Table 3.

Table 3. The proton ligand stability constants of various ligands at various temperatures.

Ligand	Temperature (° C)				
	30	40	50	60	70
1	3.88	3.70	3.56	3.41	3.27
2	3.33	3.15	3.03	2.93	2.83
3	3.54	3.40	3.29	3.20	3.10
4	3.96	3.82	3.70	3.59	3.48
5	3.63	3.49	3.36	3.25	3.14

The ΔG, ΔS and ΔH were calculated using the equations:

i) $\Delta G = 2.303RTpK$ and, ii) $\Delta S = \frac{\Delta H - \Delta G}{T}$

where the ΔH values were evaluated from the temperature coefficient method. The plots of pK against 1/T for various ligands are presented in Fig 3. The thermodynamic parameters are represented in Table 4.

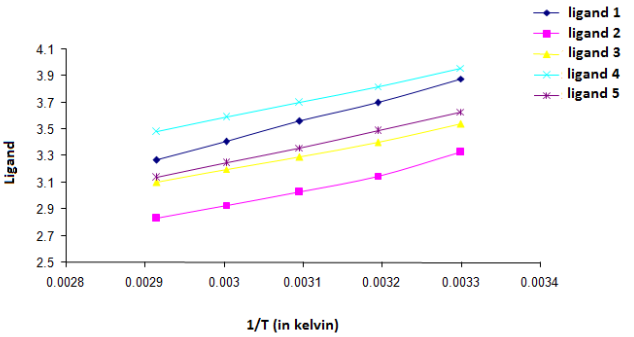
Fig. 3 The plots of pK against 1/T for various ligands.

As expected the pK values decreases with increase in the temperature for all ligands. The ΔG values are positive indicating that dissociation of ligands in to ions is thermodynamically not a favourable process. The ΔS values are negative.

The high ΔH values as compared to ΔS are responsible for complex formation process.

Table 4. Thermodynamic parameters ΔG, ΔS and ΔH

Ligand	Thermodynamic pK	+ ΔH Kcal mol^{-1}	+ΔG Kcal mol^{-1}	ΔS cal deg^{-1} mol^{-1}
1	3.88	3.684	5.3798	-5.594
2	3.33	2.7636	4.6171	-6.117
3	3.54	2.558	4.9083	-7.754
4	3.96	2.3824	5.4907	-10.25
5	3.63	2.878	5.033	-7.11



IV. CONCLUSION

The present work reports the successful synthesis of substituted thiazolyl thiosemicarbazides. The complex formation process between these substituted thiazolyl thiosemicarbazides various metal ions belonging to transition and inner transition series are investigated. These complexes follow the stability order as: Mn < Co < Ni < Cu > Zn. The obtained $logK_1$ values of Mn(II) complexes were slightly less than those of Co(II), Ni(II), Cu(II) and Zn(II); probably due to the bigger size of the thiosemicarbazide molecule causing steric hindrance in the complex formation. The experimentally calculated thermodynamic parameters explain the complex formation process.

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