Potentiometric and Thermodynamic Studies
of 3-(4-Methoxyphenyl)-5-azorhodanine Derivatives
and their Metal Complexes with Some Transition Metals. XIV

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A series of 3-(4-methoxyphenyl)-5-azorhodanine derivatives have been prepared and characterized by elemental analysis, ^{1}H NMR, and IR spectra. Proton—ligand dissociation constants of the derivatives and metal—ligand stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} ions have been determined potentiometrically in 0.1 M-KCl and 40 vol. % ethanol—water mixture. The influence of substituents on the dissociation and stability constants was examined on the basis of the electron-repelling property of the substituent. The stability constants of the formed complexes increase in the order Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}. The effect of temperature was studied and the corresponding thermodynamic parameters (ΔG, ΔH, and ΔS) were derived and discussed.

Azo compounds based on rhodanine were synthesized for the first time at the L'vov Medical Institute as potential medicinal preparations [1] and play an important role in analytical chemistry as chromogenic agents [2]. Furthermore, from a biological point of view, the study of the binding properties of organic chelating ligands containing both —N=N— and —OH groups is significant due to their use as models for certain metal—enzyme interactions and also for the possible transport of metal ions in biological media [3].

In continuation of our earlier work [4—7], we report herein the synthesis of 3-phenyl-5-azorhodanine derivatives (HL1—HL5).
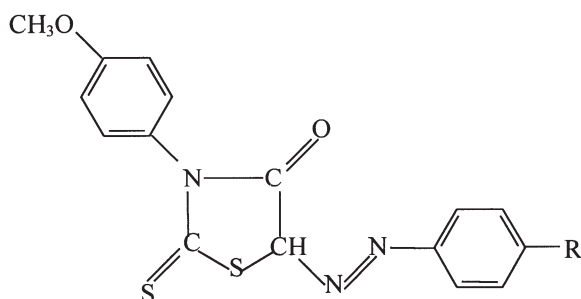

R = OCH$_3$ (HL1), CH$_3$ (HL2), H (HL3), Cl (HL4), NO$_2$ (HL5)

The synthesized ligands are characterized in Table 1.

The stability constants of Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} complexes with azorhodanines at different temperatures and substituent effects on the dissociation and stability constants are also investigated. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

The average number of protons associated with the ligands at different pH values, $\bar{n}_A$, was calculated from the titration curves of the acid in the absence and presence of a ligand. Thus, the formation curves ($\bar{n}_A$ vs. pH) for the proton—ligand systems were constructed and found to extend between 0 and 1 in the $\bar{n}_A$ scale. This means that ligands have one ionizable proton (the enolized hydrogen ion of the hydroxyl group in the rhodanine moiety). It can be seen that for the same volume of NaOH added the ligand titration curves had a lower pH value than the acid titration curve. The displacement of a ligand titration curve along the volume axis with respect to the acid titration curve is an indication of proton dissociation. The proton—ligand stability constants were calculated using the method of *Irving* and *Rossotti* [8].

The phenolic —OH group is known to be weakly acidic, indicating a stronger bonding between the proton and the oxygen donor. This means that the proton—ligand stability constant of azoquinolines

*A part of the M. Sc. Thesis.
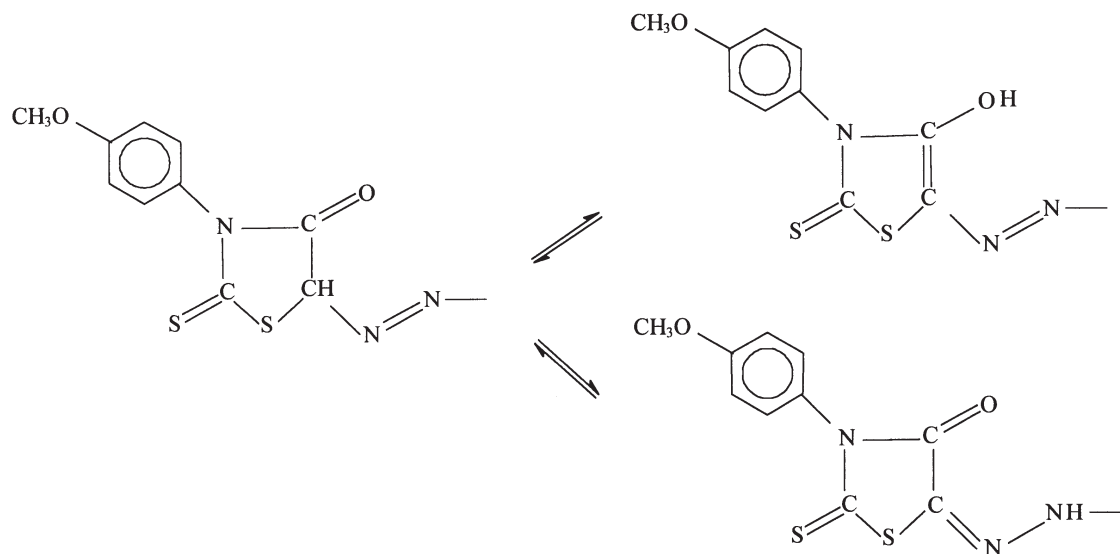
Formula 1

Table 1. Analytical Data of Azorhodanine Derivatives

| Compound[a] | Formula | M_r | w_i(calc.)/% w_i(found)/% | | | M.p. |
			C	H	N	°C
HL1	$C_{17}H_{15}N_3O_3S_2$	373.43	54.67	4.05	11.25	132
	Orange		54.55	3.97	11.15	
HL2	$C_{17}H_{15}N_3O_2S_2$	357.43	57.12	4.23	11.76	190
	Brown		57.00	4.14	11.56	
HL3	$C_{16}H_{13}N_3O_2S_2$	343.40	55.96	3.81	12.24	195
	Dark yellow		55.69	4.00	12.11	
HL4	$C_{16}H_{12}N_3O_2S_2Cl$	377.85	50.86	3.20	11.12	133
	Brown		50.66	3.12	11.00	
HL5	$C_{16}H_{12}N_4O_4S_2$	388.41	49.77	3.12	14.43	130
	Brown		49.25	3.00	14.20	

a) The analytical data agree satisfactorily with the expected formulae represented as given in structures HL1—HL5. Air-stable, coloured, insoluble in water, but soluble in hot ethanol, and soluble in coordinating solvent.

should be high due to the dissociation of the —OH group [9].

Two types of tautomerism can be suggested for the compounds HL1—HL5 as in Formula 1 [5].

An inspection of the results in Table 2 reveals that the pK^H values of HL3 and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. The p-OCH$_3$ and p-CH$_3$ derivatives (HL1 and HL2) have a lower acidic character (higher pK^H values) than the p-Cl and p-NO$_2$ derivatives (HL4 and HL5). This is quite reasonable because the presence of p-OCH$_3$ and p-CH$_3$ groups (*i.e.* an electron-donating effect) will enhance the electron density by their high positive inductive or mesomeric effect, whereby a stronger O—H bond is formed. The presence of p-Cl and p-NO$_2$ groups (*i.e.* an electron-withdrawing effect) will lead to the opposite effect.
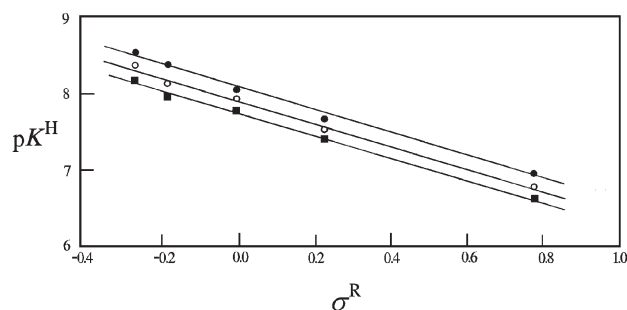

Fig. 1. Correlation of pK_1^H with Hammett's constant σ^R at 298 K (●), 308 K (○), and 318 K (■).

The results are also in accordance with Hammett's *para*-substituent constant values σ^R [10]. Straight lines are obtained on plotting pK^H values at different

Table 2. Thermodynamic Functions for the Dissociation of HL1—HL5 in 40 vol. % Ethanol—Water Mixture and 0.1 M-KCl at Different Temperatures

Compound	T/K	Dissociation constant pK_1^H	ΔG_1 kJ mol^{-1}	ΔH_1 kJ mol^{-1}	$-\Delta S_1$ J mol^{-1} K^{-1}
HL1	298	8.6	49.1	31.91	57.6
	308	8.4	49.7		57.6
	318	8.2	50.2		57.6
HL2	298	8.4	47.9	36.5	38.5
	308	8.2	48.4		38.6
	318	8.0	48.7		38.5
HL3	298	8.2	46.5	27.4	64.3
	308	8.0	47.2		64.4
	318	7.9	47.8		64.3
HL4	298	7.8	44.2	28.3	53.6
	308	7.6	44.9		54.0
	318	7.4	45.3		53.6
HL5	298	7.1	40.5	32.8	25.8
	308	6.9	40.9		26.1
	318	6.7	41.0		25.8

temperatures *vs.* σ^R (Fig. 1). The *para*-substituents in the azorhodanine moiety have a direct influence on the pK^H values of the investigated compounds, revealing the coplanarity of the molecule and thus affording a maximum resonance *via* delocalization of its π-system.

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ions ($\bar{n}$) *vs.* the free ligand exponent (pL) according to *Irving* and *Rossotti* [11]. These curves were analyzed and the successive metal—ligand stability constants were determined using different computational methods [12, 13] which agree within 1 % error. Accordingly the average values are represented in Table 3. The following general remarks can be pointed out:

i) The maximum value of $\bar{n}$ was ≈ 2 indicating the formation of 1 : 1 and 1 : 2 (metal : ligand) complexes only.

ii) The metal ion solution used in the present study was very dilute (2×10^{-5} mol dm^{-3}), hence there was no possibility of formation of polynuclear complexes [14].

iii) The metal titration curves were displaced to the right-hand side of the ligand titration curves along the volume axis, indicating proton release upon complex formation of the metal ion with the ligand. The large decrease in pH for the metal titration curves relative to ligand titration curves points to the formation of strong metal complexes [15].

iv) In most cases, the colour of the solution after complex formation was observed to be different from the colour of the ligand at the same pH.

v) For the same ligand at constant temperature, the stability of the chelates increases in the order Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} [16, 17]. This order largely reflects the changes in the heat of complex formation

across the series from a combination of the influence of both the polarizing ability of the metal ion [18] and the crystal-field stabilization energies [19]. The greater stability of Cu^{2+} complexes is produced by the well known Jahn—Teller effect.

An inspection of the results in Table 3 reveals that the stability constant values of the complexes of HL3 and its substituted derivatives are influenced by the inductive or mesomeric effect of the substituents. This behaviour correlates with the effect of substitution on the phenyl ring as follows:

i) The high stability of HL1 and HL2 complexes can be attributed to the presence of the —OCH$_3$ and —CH$_3$ groups in the *p*-position relative to the azo group, respectively. This is quite reasonable because the presence of *p*-OCH$_3$ and *p*-CH$_3$ groups (*i.e.* an electron-donating effect) will enhance the electron density by their high positive indicative or mesomeric effect, whereby stronger chelation is formed and therefore the stability of the complexes.

ii) The low stability of HL5 and HL4 complexes can be attributed to the presence of the NO$_2$ and Cl groups in the *p*-position relative to the azo group, respectively. This is caused by the negative indicative effect of the —NO$_2$ and —Cl groups which decreases their ability for chelation and therefore the stability of the complexes.

iii) For the ligands with the same metal ion at constant temperature, the stability of the chelates increases in the order HL5, HL4, HL3, HL2, HL1 [5, 20].

The dissociation constants pK^H for azoquinoline and its substituted derivatives, as well as the stability constants of their complexes with Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} have been evaluated at 298 K, 308 K, and 318 K, and are given in Tables 2 and 4. The

Table 3. Stepwise Stability Constants for ML1 and ML2 (Metal : Ligand) Complexes of the Compounds in 40 vol. % Ethanol—Water Mixtures and 0.1 M-KCl at Different Temperatures

Compound	M^{n+}	298 K		308 K		318 K	
		$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$	$\log K_1$	$\log K_2$
HL1	Mn^{2+}	6.67	5.52	6.81	5.66	6.96	5.80
	Co^{2+}	6.82	5.66	6.96	5.79	7.10	5.94
	Ni^{2+}	6.87	5.70	7.02	5.85	7.17	6.00
	Cu^{2+}	7.10	5.92	7.24	6.06	7.40	6.20
HL2	Mn^{2+}	6.55	5.41	6.70	5.56	6.86	5.70
	Co^{2+}	6.69	5.55	6.83	5.70	6.99	5.83
	Ni^{2+}	6.74	5.58	6.90	5.74	7.07	5.88
	Cu^{2+}	6.98	5.80	7.13	5.94	7.29	6.08
HL3	Mn^{2+}	6.44	5.30	6.59	5.44	6.74	5.59
	Co^{2+}	6.57	5.45	6.72	5.60	6.87	5.75
	Ni^{2+}	6.63	5.50	6.78	5.64	6.94	5.79
	Cu^{2+}	6.85	5.71	6.99	5.86	7.14	5.99
HL4	Mn^{2+}	6.20	5.14	6.31	5.30	6.45	5.44
	Co^{2+}	6.42	5.28	6.58	5.43	6.73	5.57
	Ni^{2+}	6.48	5.35	6.63	5.51	6.77	5.66
	Cu^{2+}	6.70	5.54	6.84	5.71	7.01	5.82
HL5	Mn^{2+}	6.12	4.98	6.28	5.13	6.43	5.28
	Co^{2+}	6.24	5.12	6.40	5.27	5.56	5.43
	Ni^{2+}	6.32	5.20	6.49	5.35	6.66	5.51
	Cu^{2+}	6.54	5.40	6.71	5.57	6.87	5.73

slope of the plot pK^H or $\log K$ *vs.* $1/T$ was utilized to evaluate the enthalpy change ΔH for the dissociation or complexation process, respectively. From the Gibbs energy change ΔG and ΔH values one can deduce the entropy changes ΔS using the well known relationships

$$\Delta G = -2.303RT \log K \quad \text{and} \quad \Delta S = (\Delta H - \Delta G)/T$$

All thermodynamic parameters of the dissociation process of HL3 and its derivatives are recorded in Table 2. From these results the following conclusions can be drawn:

i) The pK^H values decrease with increasing temperature, *i.e.* the acidity of the ligands increases, independently of the nature of the substituent [5].

ii) A positive value of ΔH indicates that the process is endothermic.

iii) A large positive value of ΔG indicates that the dissociation process is not spontaneous [21].

iv) The dissociation processes for HL3 and its derivatives have negative values of ΔS due to increased order as a result of the solvation processes.

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 4. It is known that the divalent metal ions exist in solution as octahedrally hydrated species [13] and the obtained values of ΔH and ΔS can then be considered as the sum of two contributions: *a*) release of H_2O molecules, and *b*) metal—ligand bond formation. Examination of these values shows that:

i) The stability constants ($\log K_1$ and $\log K_2$) for ligand complexes increase with increasing tempera-

ture, *i.e.* their stability constants increase with increasing the temperature [4].

ii) The negative value of ΔG for the complexation process suggests the spontaneous nature of such process [20].

iii) The ΔH values are positive, meaning that these processes are endothermic and favourable at higher temperature.

iv) The ΔS values for the ligand complexes are positive, confirming that the complex formation is entropically favourable [5].

EXPERIMENTAL

5-(4-Phenylazo) derivatives of 3-(4-methoxyphenyl)-2-thioxothiazolidin-4-one (HLn) were prepared. The aniline and 4-alkylanilines (alkyl: OCH_3, CH_3, Cl, and NO_2; Aldrich Chemical Co.) were used as received. The experimental technique has been described previously [5—7].

In a typical preparation, 25 cm³ of distilled water containing hydrochloric acid (0.01 mol) were added to aniline or 4-alkylaniline (0.01 mol). To the resulting mixture stirred and cooled to 0 °C, a solution of sodium nitrite (0.01 mol) in 20 cm³ of water was added dropwise. The so formed diazonium chloride was consecutively coupled with an alkaline solution of 3-(4-methoxyphenyl)-2-thioxothiazolidin-4-one (0.01 mol) in 20 cm³ of pyridine. The coloured precipitate which formed immediately was filtered and washed several times with water. The crude product was purified by recrystallization from hot ethanol, yield 65 %, then dried in vacuum desiccator over P_2O_5. The ligands

Table 4. Thermodynamic Functions for ML1 and ML2 (Metal : Ligand) Complexes of the Compounds in 40 vol. % Ethanol—Water Mixture and 0.1 M-KCl

Compound	M^{n+}	T/K	Gibbs energy change kJ mol^{-1}		Enthalpy change kJ mol^{-1}		Entropy change J mol^{-1} K^{-1}	
			$-\Delta G_1$	$-\Delta G_2$	ΔH_1	ΔH_2	ΔS_1	ΔS_2
HL1	Mn^{2+}	298	38.1	31.5			213.1	191.3
		308	39.3	32.6	25.4	25.5	210.3	188.5
		318	40.6	33.6			207.1	185.9
	Co^{2+}	298	38.9	32.3			216.2	193.9
		308	40.2	33.4	25.5	25.5	213.4	191.2
		318	41.5	34.5			210.8	188.6
	Ni^{2+}	298	39.2	32.5			223.2	200.1
		308	40.5	33.6	27.4	27.4	220.3	197.9
		318	41.8	34.7			217.3	195.1
	Cu^{2+}	298	40.5	33.8			227.7	205.2
		308	41.9	34.9	27.4	27.4	224.7	202.3
		318	43.2	36.0			221.9	199.4
HL2	Mn^{2+}	298	37.4	30.9			216.8	192.2
		308	38.6	31.9	27.3	26.4	213.9	189.4
		318	39.9	32.9			211.1	186.7
	Co^{2+}	298	38.2	31.7			219.8	195.2
		308	39.5	32.7	27.4	26.5	216.8	192.3
		318	40.7	33.8			214.0	189.6
	Ni^{2+}	298	38.5	31.8			223.2	198.5
		308	39.7	32.9	28.1	27.4	220.1	195.6
		318	41.0	34.0			217.3	192.8
	Cu^{2+}	298	39.7	33.1			228.0	202.0
		308	41.0	34.2	28.3	27.4	225.0	200.0
		318	42.4	35.3			222.0	197.0
HL3	Mn^{2+}	298	36.7	30.2			215.0	190.2
		308	38.0	31.3	27.4	26.4	212.0	187.3
		318	39.2	32.3			209.3	184.6
	Co^{2+}	298	37.5	31.1			217.5	195.9
		308	38.7	32.1	27.4	27.4	214.5	193.1
		318	40.0	33.2			211.7	190.3
	Ni^{2+}	298	37.8	31.4			221.7	197.3
		308	39.1	32.4	28.3	27.4	218.6	194.3
		318	40.4	33.5			215.7	191.5
	Cu^{2+}	298	39.1	32.6			226.5	201.6
		308	40.4	33.7	28.4	27.5	223.4	198.6
		318	41.7	34.8			220.5	195.8
HL4	Mn^{2+}	298	35.9	29.3			197.0	186.8
		308	37.2	30.3	22.8	26.4	194.6	183.9
		318	38.4	31.3			192.2	181.2
	Co^{2+}	298	36.6	30.1			223.9	189.7
		308	37.9	31.1	25.3	26.4	204.9	186.9
		318	39.1	32.1			202.3	184.2
	Ni^{2+}	298	37.0	30.5			212.5	197.2
		308	38.2	31.6	26.4	28.3	209.9	194.1
		318	39.5	32.6			207.2	191.2
	Cu^{2+}	298	38.2	31.6			223.0	201.7
		308	39.5	32.7	28.3	28.5	220.0	198.6
		318	40.8	33.7			217.0	195.7
HL5	Mn^{2+}	298	34.9	28.4			211.9	180.4
		308	36.1	29.4	28.3	25.4	208.9	177.6
		318	37.3	30.3			206.0	175.0
	Co^{2+}	298	35.6	29.2			217.3	186.1
		308	36.8	30.2	29.2	26.3	214.1	183.2
		318	38.0	31.2			211.1	180.5
	Ni^{2+}	298	36.1	29.7			221.6	187.6
		308	37.3	30.7	30.0	26.3	218.3	184.8
		318	38.5	30.9			215.3	179.6
	Cu^{2+}	298	37.3	30.8			226.1	194.2
		308	38.6	31.8	30.1	27.1	222.8	191.2
		318	39.8	32.9			219.8	188.5

were also characterized by elemental analysis (Table 1), ^{1}H NMR and IR spectroscopy.

Metal ion solutions (0.0002 mol dm^{-3}) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA [22]. The ligand solutions (0.001 mol dm^{-3}) were prepared by dissolving the accurate mass of the solid in ethanol (Analar). Solutions of 0.001 M-HCl and 1 M-KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 40 vol. % ethanol—water mixture was used as titrant and standardized against oxalic acid (Analar).

The apparatus, general conditions, and methods of calculation were the same as in the previous works [5—7]. The following mixtures were prepared and titrated potentiometrically at 298 K against standard 0.005 M-NaOH in 40 vol. % ethanol—water mixture:

i) 5 cm^3 0.001 M-HCl + 5 cm^3 1 M-KCl + 20 cm^3 ethanol,

ii) 5 cm^3 0.001 M-HCl + 5 cm^3 1 M-KCl + 15 cm^3 ethanol + 5 cm^3 0.00l M-ligand,

iii) 5 cm^3 0.001 M-HCl + 5 cm^3 l M-KCl + 15 cm^3 ethanol + 5 cm^3 0.001 M-ligand + 5 cm^3 0.0002 M-metal salt.

For each mixture, the volume was made up to 50 cm^3 with bidistilled water before the titration. These titrations were repeated for temperatures of 308 K and 318 K. A constant temperature was maintained at $\pm$ 0.05 K by using an ultrathermostat (Neslab 2 RTE 220). The pH measurements were carried out using VWR Scientific instruments model 8000 pH-meter accurate to $\pm$ 0.01 units. The pH-meter readings in 40 vol. % ethanol—water mixture are corrected according to the *Van Uitert* and *Hass* relation [23].

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