Potentiometric and Conductometric Studies on the Complexes of Some Transition Metals with Rhodanine Azosulfonamide Derivatives. XI

[a]A. T. MUBARAK, [b]A. Z. EL-SONBATI*, and [b]A. A. EL-BINDARY*

[a]*Department of Chemistry, Faculty of Science, King Khalid University, P.O.Box 9004, Abha 61413, Saudi Arabia*

[b]*Department of Chemistry, Faculty of Science (Demiatta), Mansoura University, Demiatta, Egypt*
e-mail: ahmadtahir20@hotmail.com

Received 29 September 2003

Stability constants of bivalent (Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) metal ion complexes with rhodanine azosulfonamide derivatives have been determined potentiometrically in 0.1 M-KCl and 30 vol. % ethanol—water mixture. The stability constants of the formed complexes increase in the order Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}. The influence of substituents on the stability of the complexes was examined on the basis of electron repelling property of the substituent. The effect of temperature on the stability of the complexes formed was studied and the corresponding thermodynamic quantities (ΔG, ΔH, and ΔS) were derived and discussed. The stoichiometries of these complexes were determined conductometrically and indicated the formation of 1:1 and 1:2 (n(metal):n(ligand)) complexes.

Much interest has been shown in the chemistry of sulfonamide antibacterials with respect to their biological activities [1]. Rhodanines have been extensively investigated by organic chemists due to their close association with various types of biological activities [2]. They are also of particular interest because of their use as local anesthetics [3]. Drug log K values can be used to predict possible precipitation in admixtures and solubilities in aqueous solutions as well as to provide optimum bioavailability by maintaining a certain ratio of ionized to unionized drug [4]. In continuation to the earlier works [5—7], we report herein the stability constants of Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} complexes with rhodanine azosulfonamide derivatives at different temperatures and the corresponding thermodynamic quantities of complexation are evaluated and discussed. Moreover, the stoichiometries of these complexes are determined conductometrically at 298 K.

EXPERIMENTAL

Ligands of *N*-substituted 4-[(4-oxo-3-phenyl-2-thioxothiazolidin-5-yl)azo]benzenesulfonamides *I*—*V* and their derivatives were prepared as previously described [5—8]. Their purities were checked by elemental analyses, IR, and ^{1}H NMR spectra.

Metal ion solutions (0.001 mol dm^{-3}) were prepared from Analar metal chlorides in bidistilled water and standardized with EDTA [9]. The ligand solutions (0.01 mol dm^3) were prepared by dissolving the accurate mass of the solid in ethanol (Analar). Solutions of 0.005 M-HCl and 1 M-KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 30 vol. % ethanol—water mixture was used as titrant and standardized against oxalic acid (Analar).

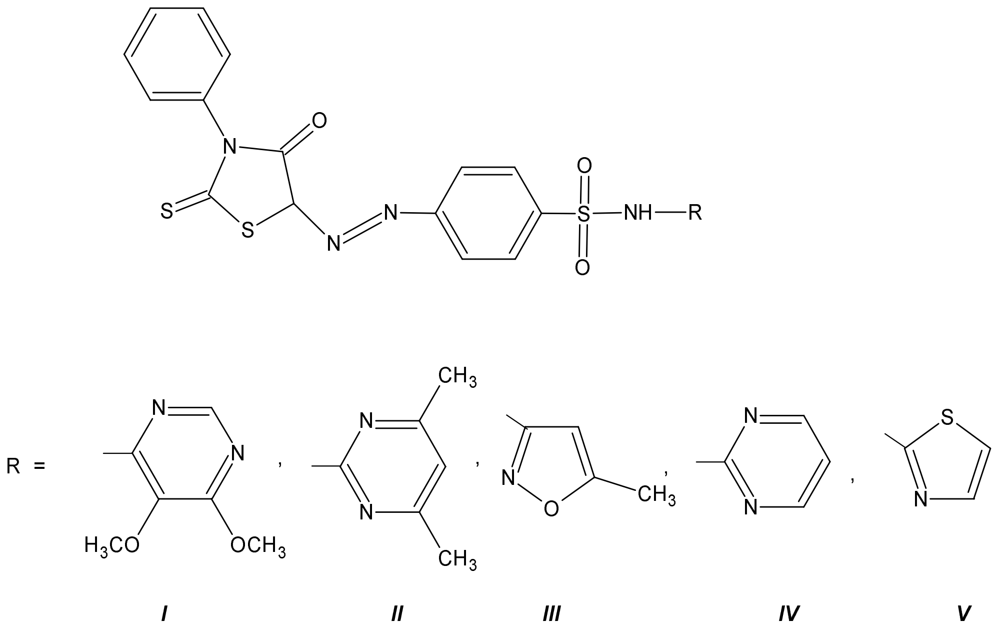
The potentiometric measurements, apparatus, general conditions, and methods of calculation were the same as in the previous works [5—7]. The following mixtures were prepared and titrated potentiometrically at 298 K against the standard 0.02 M-NaOH in 30 vol. % ethanol—water mixture:

i) 5 cm^3 0.005 M-HCl + 5 cm^3 1 M-KCl + 15 cm^3 ethanol;
ii) 5 cm^3 0.005 M-HCl + 5 cm^3 1 M-KCl + 10 cm^3 ethanol + 5 cm^3 0.01 M-ligand;
iii) 5 cm^3 0.005 M-HCl + 5 cm^3 1 M-KCl + 10 cm^3 ethanol + 5 cm^3 0.01 M-ligand + 10 cm^3 0.001 M-metal chloride.

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 to ± 0.05 K by using an ultrathermostat (Neslab 2 RTE 220). The pH measurements were carried out using VWR

---

*[*]*Present address*: Department of Chemistry, Faculty of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia.



Scientific instruments model 8000 pH-meter accurate to ± 0.01 units. The pH-meter readings in 30 vol. % ethanol—water mixture are corrected according to the *Van Uitert* and *Hass* relation [10].

The conductometric measurements solutions of 10^{-4} M-metal chloride were titrated with 10^{-3} M-ligand. These titrations were performed using YSI model 32 conductivity meter at 298 K.

RESULTS AND DISCUSSION

The values of both the deprotonation constants and their thermodynamic functions for the ligands studied in this work were as those previously reported [5]. 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 stability constants were determined using different computational methods [12, 13] and they agree within 1 % error. Accordingly the average values are represented in Table 1. The following general remarks can be pointed out:

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

– The metal ion solution used in the present study was very dilute (10^{-4} mol dm^{-3}), hence there was little possibility of polynuclear complexes formation [14].

– 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].

– 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.

– For the same ligand at constant temperature, the stability of the chelates decreases in the order Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} [7, 16, 17]. This order largely reflects the changes in the heat of complex formation across the series from combination of the influence of both polarizing ability of the metal ion [18] and 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 1 reveals that the stability constant values of the complexes of rhodanine azosulfonamide derivatives are influenced by the inductive or mesomeric effect of the substituents [5, 6]. This behaviour correlates with the effect of different sulfa drugs as follows:

– The high stability of *I* and *II* complexes can be attributed to the presence of —OCH_3 and —CH_3 group in the *p*-position relative to the azo group, respectively. This is quite reasonable because the presence of the above groups (*i.e.* an electron-donating effect) will enhance the electron density by their high positive indicative or mesomeric effect, whereby stronger chelation was formed.

– The low stability of *IV* and *V* complexes can be attributed to the absence of —OCH_3 and —CH_3 group. This is caused by the negative indicative effect which decreases their ability for chelation and therefore the stability of the complexes.

– For the ligands with the same metal ion at con-

Table 1. Stepwise Stability Constants for the Complexation of Rhodanine Azosulfonamides with Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} in 30 vol. % Ethanol—Water Mixture and 0.1 M-KCl at Different Temperatures

Ligand	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
I	Mn^{2+}	6.40	4.40	6.60	4.62	6.80	4.84
	Co^{2+}	6.80	4.92	6.98	5.10	7.16	5.28
	Ni^{2+}	7.25	5.42	7.45	5.64	7.65	5.86
	Cu^{2+}	7.62	5.82	7.82	6.00	8.00	6.22
II	Mn^{2+}	5.87	3.56	6.10	3.76	6.32	3.98
	Co^{2+}	6.82	3.66	7.03	3.88	7.25	4.20
	Ni^{2+}	7.50	4.30	7.72	4.50	7.95	4.70
	Cu^{2+}	7.70	4.50	7.92	4.72	8.15	4.95
III	Mn^{2+}	6.35	3.58	6.50	3.70	6.70	3.83
	Co^{2+}	6.50	3.60	6.75	3.85	7.00	4.09
	Ni^{2+}	6.60	3.63	6.80	3.90	7.05	4.15
	Cu^{2+}	6.72	3.65	6.94	4.00	7.19	4.25
IV	Mn^{2+}	7.65	4.60	7.40	4.40	7.20	4.20
	Co^{2+}	7.80	4.68	7.52	4.46	7.30	4.24
	Ni^{2+}	7.85	4.72	7.60	4.58	7.40	4.40
	Cu^{2+}	8.00	5.00	7.70	4.80	7.50	4.46
V	Mn^{2+}	6.60	3.60	6.82	3.80	7.00	4.00
	Co^{2+}	6.80	3.82	7.00	4.00	7.22	4.25
	Ni^{2+}	7.03	4.00	7.25	4.25	7.40	4.50
	Cu^{2+}	7.30	4.20	7.50	4.50	7.70	5.00

Table 2. Thermodynamic Functions for the Complexation of Rhodanine Azosulfonamides in 30 vol. % Ethanol—Water Mixture at 298 K

Ligand	M^{n+}	$\frac{-\Delta G_j}{\text{kJ mol}^{-1}}$		$\frac{\Delta H_j}{\text{kJ mol}^{-1}}$		$\frac{\Delta S_j}{\text{J mol}^{-1}\text{ K}^{-1}}$	
		1	2	1	2	1	2
I	Mn^{2+}	36.52	25.11	31.02	36.38	266.64	206.34
	Co^{2+}	38.81	28.08	36.38	31.79	252.32	200.91
	Ni^{2+}	41.36	30.92	35.84	30.44	259.06	205.91
	Cu^{2+}	43.47	33.21	36.37	31.78	267.92	218.09
II	Mn^{2+}	27.78	20.31	38.29	33.29	222.71	179.86
	Co^{2+}	33.21	20.88	34.80	31.91	228.22	177.14
	Ni^{2+}	37.09	24.53	36.47	33.30	246.84	194.06
	Cu^{2+}	38.80	25.67	42.54	35.29	272.90	204.56
III	Mn^{2+}	36.23	20.42	30.06	20.12	222.40	136.10
	Co^{2+}	37.03	20.54	45.05	19.17	275.40	133.15
	Ni^{2+}	37.66	20.71	30.63	17.23	229.12	127.32
	Cu^{2+}	38.34	20.82	42.12	27.70	270.00	162.82
IV	Mn^{2+}	43.64	26.24	41.81	28.29	286.74	182.99
	Co^{2+}	44.51	26.70	42.86	27.86	293.19	183.09
	Ni^{2+}	44.79	26.93	41.79	25.95	290.54	177.45
	Cu^{2+}	45.64	28.52	43.59	23.22	299.43	173.62
V	Mn^{2+}	37.66	20.54	34.81	34.81	243.18	185.73
	Co^{2+}	38.80	24.54	43.85	35.90	277.34	202.81
	Ni^{2+}	48.24	22.82	30.63	43.51	264.66	222.58
	Cu^{2+}	41.05	23.96	34.81	43.51	256.57	226.41

stant temperature, the stability of the chelates decreases in the order *I*, *II*, *III*, *IV*, *V* [6].

Stability constants of the complexes of ligands studied 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 Table 1. The slope of the plot (log K *vs.* $1/T$) was utilized to evaluate the enthalpy change (ΔH) for the complexation process. From the Gibbs energy change (ΔG) and (ΔH) values one can deduce the entropy changes (ΔS) using the well known relationships

$$\Delta G = -2.303\, RT \log K \qquad (1)$$

$$\Delta S = (\Delta H - \Delta G)/T \qquad (2)$$

All the thermodynamic parameters of the stepwise stability constants of complexes are recorded in Table 2. It is known that the divalent metal ions exist in solution as octahedrally hydrated species and the obtained values of ΔH and ΔS can then be considered as a sum of two contributions: *a*) release of H_2O molecules, and *b*) metal—ligand bond formation. Examination of these values shows that:

– The stepwise stability constants ($\log K_1$ and $\log K_2$) for ligand complexes increase with increasing temperature, *i.e.* their stability constants increase with increasing the temperature.

– The negative value of ΔG for the complexation process suggests a spontaneous nature of such process [6, 20].

– The ΔH values are positive, *i.e.* these processes are endothermic and favourable at higher temperature.

– The ΔS values for the ligand complexes are positive confirming that the complex formation is entropically favourable.

Stoichiometries of the complexes of ligands with Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} result from the conductometric measurements. These studies were carried out to investigate the stoichiometries of the formed complexes by breaks denoting the formation of 1:1 and 1:2 (n(metal):n(ligand)) complexes. Therefore, the relation between the metal ions and ligand occurs *via* the formation of a covalent linkage with the oxygen of the —OH group (rhodanine moiety) and the nitrogen of the azo group [6]. The increase in conductance upon titrating metal ions by ligand is probably due to the liberation of the hydrogen ions from the —OH group during the complex formation [21]. The decrease of the conductance value occurs due to *i*) the increase of the volume of the metal ion chelate formation which is accompanied by the decrease in the value of diffusion coefficient of the particle, and *ii*) the lowering of the charge on the metal ion through covalent bond formation with ligand.

REFERENCES

1. Goodman, L. S. and Gilman, A., *The Pharmacological Basis of Therapeutics*, 4th Edition. Academic Press, London—New York, 1972.
2. Kidwai, M., Bala, R., and Kumar, K., *Indian J. Pharm. Sci. 57*, 252 (1995).
3. Troulman, H. D. and Long, L. M., *J. Am. Chem. Soc. 70*, 3486 (1948).
4. Kosanic, M., Kapetanovic, V., Milovanovic, L., Buric, N., and Veselinovic, D., *Monatsh. Chem. 128,* 137 (1997).
5. El-Bindary, A. A., El-Sonbati, A. Z., El-Mosalamy, E. H., and Ahmed, R. M., *Chem. Pap. 57*, 255 (2003).
6. El-Sonbati, A. Z., El-Bindary, A. A., and Ahmed, R. M., *J. Solution Chem. 32*, 617 (2003).
7. Mubarak, A. T., *J. Solution Chem. 33*, 149 (2004); *33*, 1041 (2004).
8. El-Dissouky, A., El-Bindary, A. A., El-Sonbati, A. Z., and Hilali, A. S., *Spectrochim. Acta, Part A 57*, 1163 (2001).
9. Jeffery, G. H., Bassett, J., Mendham, J., and Deney, R. C., *Vogel's Textbook of Quantitative Chemical Analysis*, 5th Edition. Longman, London, 1989.
10. Van Uitert, L. G. and Hass, C. G., *J. Am. Chem. Soc. 75*, 451 (1953).
11. Irving, H. and Rossotti, H. S., *J. Chem. Soc. 1953*, 3397.
12. Rossotti, F. J. C. and Rossotti, H. S., *Acta Chem. Scand. 9*, 1166 (1955).
13. Beck, M. T. and Nagybal, I., *Chemistry of Complex Equilibrium.* Wiley, New York, 1990.
14. Sanyal, P. and Sengupta, G. P., *J. Indian Chem. Soc. 67*, 342 (1990).
15. Athawale, V. D. and Lele, V., *J. Chem. Eng. Data 41*, 1015 (1996).
16. Ibañez, G. A. and Escandar, G. M., *Polyhedron 17*, 4433 (1998).
17. Athawale, V. D. and Nerkar, S. S., *Monatsh. Chem. 131*, 267 (2000).
18. Harlly, F. R., Burgess, R. M., and Alcock, R. M., *Solution Equilibria*, p. 257. Ellis Horwood, Chichester, 1980.
19. Phillips, C. S. G. and Williams, R. J. P., *Inorg. Chem.* (Oxford) *2*, 268 (1966).
20. Bebot-Bringaud, A., Dange, C., Fauconnier, N., and Grard, C., *J. Inorg. Biochem. 75*, 71 (1999).
21. El-Bindary, A. A., El-Sonbati, A. Z., and Kera, H. M., *Can. J. Chem. 77,* 1305 (1999).