ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 1, pp. 73–75. © Pleiades Publishing, Ltd., 2009.
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The Effect of Temperature on the Formation of Bismuth(III) Monocysteine and Monothiosemicarbazide Complexes

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Received February 18, 2008

Abstract—The stability constants of monocomplexes of cysteine (H_2Cys) and thiosemicarbazide (Tsc) with bismuth(III) at 288, 313 and 333 K in 0.5 M $HClO_4$ and an ionic strength of 2($NaClO_4$) were determined by spectrophotometry. On the basis of a substantial difference in the stability constants of bismuth monocomplexes with H_2Cys and Tsc, the high acidity of the investigated solutions, and known coordination modes of these ligands in crystalline compounds, the formation of Bi(HCys–O,S)$^{2+}$ and Bi(Tsc–N, S)$^{3+}$ is suggested.

DOI: 10.1134/S107032840901014X

Bismuth compounds possess antimicrobial and anticarcinogenic activity. They are used in treating such infectious diseases as syphilis, malaria, diarrhea, etc. [1]. The medical properties of bismuth in many respects are determined by its complexation in a water solution, for example, with N,S-donor ligands, which possess a wide range of biological activity, in particular, derivatives of thiosemicarbazide [2]. The interaction of bismuth(III) with L-cysteine and glutathione is of great value [1].

Despite the fact that the medical properties of bismuth compounds were known in the Middle Ages, it is necessary to ascertain their lesser level of scrutiny in the solid state and especially in solution in comparison to other biometals. So, there are few data on the interaction of bismuth(III) with L-cysteine (**H_2Cys**) [3] and thiosemicarbazide (Tsc) in water solutions [4].

In the present work, the equilibrium constants of the formation of monocysteine and monothiosemicarbazide bismuth(III) complexes at 288, 313, and 333 K in the presence of 0.5M $HClO_4$ and an ionic strength ***I*** of 2($NaClO_4$).

EXPERIMENTAL

Preparation and analysis of initial solutions of $Bi(ClO_4)_3$, $NaClO_4$, and H_2Cys have been described earlier [3]. Tsc was of chemically pure grade and additionally purified by recrystallization from a water solution.

The optical density of the working solutions was measured in a wavelength range of 260–300 nm on an Evolution 300 scanning spectrophotometer (ThermoChem, United States) with quartz cells (l = 1 cm). To prevent bismuth(III) from hydrolysis, the solution was acidified to 0.5 M $HClO_4$ and the ionic strength was maintained by $NaClO_4$. The temperature of solutions was kept constant using a Haake DC10 thermostat.

The concentration of Bi(III) was varied from 0.001 to 0.01 mol/l; c_{Cys} and c_{Tsc} were 0.0001 mol/l.

RESULTS AND DISCUSSION

In the UV spectrum of bismuth(III) solutions with H_2Cys or Tsc, bands with maxima at 263 nm appear that were absent in the spectra of solutions of separate reagents, the position of which does not change as c_{Bi} varies. This data together with the condition of $c_{\mathrm{Bi}} \gg c_{\mathrm{Cys}}$ or c_{Tsc} point to the formation of only the corresponding mononuclear monocoordinated complexes under conditions studied.

From the spectral data, we calculated the change in the optical density of solution (**ΔA**) due to the formation of bismuth complexes with H_2Cys or Tsc [3]. Figures 1 and 2 show the dependences of ΔA on the wavelength (λ, nm) obtained for H_2Cys and Tsc at 288 and 313 K, respectively. These dependences have a similar character at other temperatures.

The conditional stability constants of monocomplexes ($\boldsymbol{\beta}_1^*$) at l = 1 cm were calculated by the equation [5]

$$\frac{\Delta A}{c_{Bi}} = \varepsilon_1 \beta_1^* c_{\mathrm{L}} - \beta_1^* \Delta A,$$

where ε_1 is the molar extinction coefficient of a complex and c_{L} is the analytical concentration of a ligand. The values of β_1^*, calculated as the slope of a straight line in coordinates of $\Delta A/c_{Bi}$–ΔA from data obtained at two λ, are presented in the table. Constants obtained at other λ coincided with the data in the table within a confidence interval of (ρ = 0.95). The ε_1 values of com-

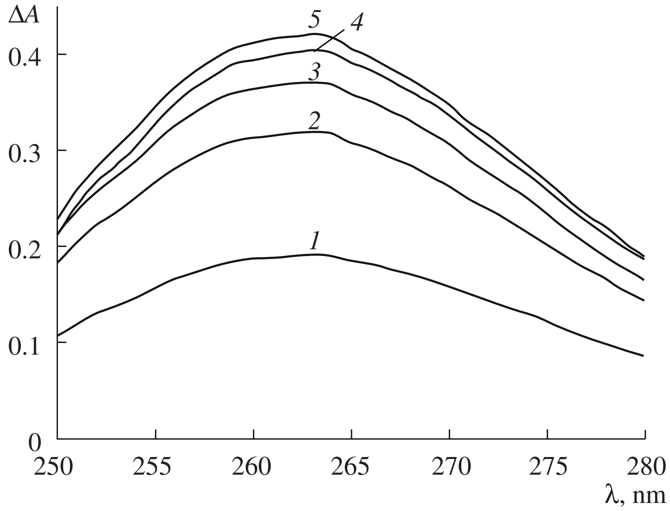

Fig. 1. Dependences of ΔA on λ in the formation of the monocysteine complex: $c_{\mathrm{Bi}} = 1.00$ (*1*), 3.00 (*2*), 5.00 (*3*), 7.00 (*4*), and 9.00 mmol/l (*5*); $c_{\mathrm{Cys}} = 1 \times 10^{-4}$ mol/l; 288 K.

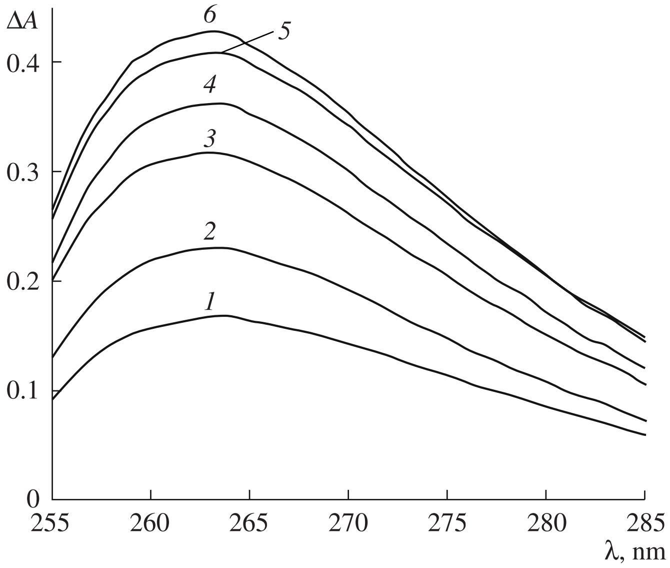

Fig. 2. Dependences of ΔA on λ in the formation of the monothiosemicarbazide complex: $c_{\mathrm{Bi}} = 1.02$ (*1*), 1.53 (*2*), 2.55 (*3*), 4.07 (*4*), 5.09 (*5*), and 7.64 mmol/l (*6*); $c_{\mathrm{Tsc}} = 1 \times 10^{-4}$ mol/l; 313 K.

plexes were found from intercepts $\varepsilon_1 \beta_1^* c_L$. At 263 nm, they were 5.9×10^3 for thiosemicarbazide and 4.8×10^3 for cysteine complexes.

H_2Cys and Tsc are multifunctional ligands. In the Cambridge Structural Database (CSD) [6], the structures of only two complexes of these ligands with bismuth(III) are described. In $[Bi(H_2O)(Phen\text{-}N,N')(NO_3)(HCys\text{-}O,S)](NO_3)$ (Phen = phenanthroline), the ligand binds through a sulfur atom of the thiol group and an oxygen atom of the carboxyl group. In $[Bi_3(\mu_3\text{-}Cl)(Tsc\text{-}N,S)_3Cl_9]_2[Bi(Tsc\text{-}N,S)_3]_2[BiCl_6]Cl$, consisting of three complex fragments, Tsc coordinates through nitrogen and sulfur atoms. Complexes with neutral thiosemicarbazide molecules are usually formed in an acidic medium. In the presence of bases, compounds with a deprotonated ligand are formed [2].

To calculate the intrinsic stability constants ($\boldsymbol{\beta_1}$), it is necessary to take into account the protonation of ligands. The protonation constants of $HCys^-$ were calculated from the correlation relationships obtained for the solutions of H_2Cys in NaCl [7]. It was assumed that, in the presence of chloride and perchlorate under the condition I = const, they are approximately the same. The equilibrium of the addition of a third proton to the noncoordinating NH_2 group with the formation of NH_3^+ (H_3Cys^+)was not taken into consideration, since the assumption that this ligand is tridentate (N,O,S-coordination) results in an anomalously high value of β_1 (10^{21}) and does not agree with the structure given in the CSD. The dependence $\ln\beta_1$–$1/T$ was used to find the values of ΔH (–45 kJ/mol) and ΔS (89 J/mol K) for the complex formation reaction.

Conditional stability constants of bismuth(III) monocomplexes with L-cysteine and thiosemicarbazide in 0.5 M $HClO_4$ at $I = 2$ ($NaClO_4$) and T = 288, 313, and 333 K

Ligand	λ, nm	$\log\beta_1^*$		
		288 K	313 K	333 K
H_2Cys	263	2.80 ± 0.02	2.73 ± 0.05	2.62 ± 0.06
	270	2.80 ± 0.02	2.74 ± 0.05	2.68 ± 0.05
Mean value $\log\beta_1^*$		2.81	2.73	2.65
Tsc	263	2.84 ± 0.07	2.61 ± 0.06	2.47 ± 0.08
	280	2.82 ± 0.03	2.61 ± 0.06	2.51 ± 0.08
Mean value $\log\beta_1^*$		2.83	2.61	2.49

As follows from the table, with an increase in temperature, the stability of bismuth(III) complexes with cysteine and thiosemicarbazide decreases, which evidences that complex formation is exothermic. The formation of a monocysteine complex is favored by both thermodynamic factors, but the enthalpy plays a greater role. The rather high stability of a complex and positive changes in entropy testify to the formation of a chelate and the bidentate ligand binding. In the absence of literature data on the temperature dependence of the Tsc protonation constant, we were able to estimate only β_1 for the Bi(III)–Tsc system, assuming a ligand protonation constant of ~10^2 [4]. In the considered temperature range, $\log\beta_1 \approx 5$. This value is 3–4 orders higher than for thiourea or its derivatives [4], which indicates chelate N,S-binding of a ligand [2]. The increased stability of a monocysteine complex ($\log\beta_1 = 12.9$, 12.2, and 11.8 at T = 288, 313 and 333 K, respectively) in comparison with monothiosemicarbazide ($\Delta\log\beta_1 \approx 7$) can be explained by the participation of an oxygen atom along with an sulfur atom in the coordination of the ligand.

Earlier [3], on the basis of IR spectral analysis, we assumed that in $Bi(HCys)_3$, the ligand is bound with bismuth through sulfur and nitrogen atoms. This compound was isolated from neutral and weak acidic solutions (pH 3–7), when protonation of the NH_2 group is less pronounced. Due to the necessity of suppressing bismuth(III) hydrolysis, the formation of the monocysteine complex was studied in 0.5 M $HClO_4$. In these conditions, ligand coordination via a nitrogen atom becomes less probable.

On the basis of a substantial difference in the stability constants of bismuth monocomplexes with H_2Cys and Tsc, and the known modes of coordination of these ligands in solid compounds and the high acidity of the studied solutions, it is possible to assume that cysteine forms $Bi(Cys\text{-}O,S)^{2+}$ and thiosemicarbazide forms $Bi(Tsc\text{-}N,S)^{3+}$.

This study of bismuth complex formation with H_2Cys and Tsc in a water solution confirms the chelate character of the complexes obtained (O,S- and O,N-type of binding of cysteine and thiosemicarbazide, respectively), found for complexes in the solid state.

This work was supported by the Russian Foundation for Basic Research and the Krasnoyarsk Regional Science Foundation (grant no. 07-03-96805).

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