

Factors affecting copper(II) reduction in aqueous solutions containing glycine

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Investigation of the reaction of glycine with Cu(II) in strongly acidic aqueous solutions showed that in the presence of Cl⁻ ions a redox process occurs, accompanied by separation from concentrated aqueous solutions of glossy black-green crystals containing both Cu(II) and Cu(I). The composition of crystals depends on the way of their preparation. Chemical analysis led to identification of compounds Cu₂Cl₃·2gly (gly = glycine, aminoacetic acid) and Cu₃Cl₅·4gly. Experimental results obtained pointed out that the observed reduction of Cu(II) is connected with a mutual influence of ligands in the coordination sphere of Cu(II) complexes.

При исследовании реакций глицина с двухвалентной медью в очень кислых средах обнаружено, что в присутствии хлоридных анионов Cl⁻ протекает окислительно-восстановительная реакция, в следствии которой из растворов получают черно-зеленые блестящие кристаллы, содержащие одно- и двухвалентную медь. Химический состав кристаллов меняется в зависимости от способа их приготовления, химическим анализом идентифицированы соединения Cu₂Cl₃·2gly и Cu₃Cl₅·4gly (gly = глицин). Исходя из экспериментальных данных можно прийти к выводу, что восстановление Cu(II) надо связывать с взаимным влиянием лигандов в координационной сфере комплексов двухвалентной меди.

It is known that Cu(II) complexes containing in the coordination sphere ligands with different σ -donating or π -accepting ability, undergo in solutions spontaneous redox changes [1, 2]. In some cases, the ligand linked to the central atom through a $>C=O$ group acted as a π acceptor [2]. Simultaneous coordination of Cu(II) with the carbonyl oxygen and the nitrogen atom of *N*-benzoylhydrazine (L) was found in a copper(I)—copper(II) complex of the composition Cu₄Cl₅L₂ [3]. Relatively little attention was devoted to complex-forming reactions of amino acids in strongly acidic medium. Not even the papers in which the stability constants of

the formed complexes were determined [4, 5] dealt with the coordination mode of the protonated amino acids to the central atom.

It was of interest to examine, whether the reduction of Cu(II) to Cu(I) could be achieved in heterogeneous Cu(II)—amino acid complexes by suitable combination of ligands in the coordination sphere. This interest was substantiated particularly because the reduction of Cu(II) to Cu(I) in the complex $\text{Cu}(\text{gly})_2$ could be induced by ultraviolet light in solutions of pH ranging from 3.5 to 7.5 [6]. The complex $\text{Cu}_2\text{Cl}_3(\text{gly})_2$ has also been prepared [7]. In this complex the carboxyl groups of glycine form with the Cu(II) atom binuclear species of the type of cupric acetate $[\text{Cu}_2(\text{NH}_3^+\text{CH}_2\text{COO}^-)_4]^{4+}$ while the chlorine atoms are coordinated to Cu(I) in the $[\text{Cu}_2\text{Cl}_6]^{4-}$ ion. However, the conditions of the Cu(II) to Cu(I) reduction have not been studied yet. The aim of the present work was to examine the reactions proceeding between Cu(II) and glycine in strongly acidic aqueous medium in the presence of Cl^- , SO_4^{2-} , and ClO_4^- ions and to find out how these ions influence the Cu(II) reduction in the studied systems.

Experimental

Reagents

Solutions were prepared using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, glycine, α - and β -alanine, hydrochloric, sulfuric, and perchloric acids, all of anal. grade, and freshly distilled ethanalamine.

Equipment

A Specord UV VIS 200 (Zeiss, Jena) spectrophotometer was used.

Analytical procedures

The total content of copper in the complexes was determined after precipitation of copper in solutions of the analyzed samples with sodium sulfide, solubilization of the precipitate in aqua regia followed by neutralization, by complexometric titration using murexide as indicator. The chloride content was determined by potentiometric titration and the composition of the used acids by alkaline titration methods. The content of carbon, nitrogen, and hydrogen in the studied complexes was determined by elemental analysis with an automatic CHN analyzer (C. Erba, Milan).

A spectrophotometric method [8] was used to estimate Cu(II) in the presence of Cu(I) since the occurrence of both copper oxidation states was indicated by analysis of black-green complexes (Table 1). The method is based on the formation of yellow chlorocopper(II) complexes in acetone absorbing in the visible spectral region ($\lambda_{\text{max}} = 476 \text{ nm}$) while the chlorocopper(I) complexes are in this region transparent. The analyzed samples were dissolved in a solution of lithium chloride in acetone to give a $\text{Cl}^- : \text{Cu}$ ratio higher than 70.

Table 1

Composition of some prepared complexes

Compound	<i>M</i>	% Cu _{total}	% Cu(II)	% Cu(I)	% Cl	% C	% H	% N
Cu ₂ Cl ₃ ·2(gly) (calc)	383.59	33.13	16.57	16.57	27.72	12.51	2.63	7.30
<i>II</i> (found)		33.00	16.42	16.58	27.37	11.66	2.66	6.98
<i>VI</i> (found)		30.49	14.94	15.55	26.92	11.83	2.60	7.04
Cu ₃ Cl ₅ ·4(gly) (calc)	668.18	28.53	19.02	9.51	26.53	14.36	3.02	8.38
<i>III</i> (found)		29.75	20.00	9.75	25.67	12.47	2.85	7.49
Cu ₃ Cl ₄ ·4(gly)·5H ₂ O (calc)	718.76	26.52			19.73	13.35	3.93	7.79
<i>IV</i> (found)		26.61			19.88	12.49	3.30	7.47

The content of Cu(II) was learned from a calibration curve and the Cu(I) content was found as a difference between the total copper and Cu(II). In the presence of glycine this method is applicable up to 10^{-3} mol l⁻¹ copper concentration. A blue precipitate, forming at higher copper concentrations, interferes with the determination.

Preparation of solutions and complexes: composition of the starting solutions, temperatures of their concentration, and qualitative description of reaction products are presented in Table 2.

Results and discussion

The main subject of our interest was the reduction of Cu(II) to Cu(I), occurring in strongly acidic aqueous solution of the system containing glycine and chlorides. From such solutions copper(I)—copper(II) complexes are separated, most often in the form of black-green glossy crystals. The composition of these compounds (e.g. *II*, *III*, and *VI*) is, to a certain degree, variable. With the decreasing content of Cu(I) in the complexes (Table 1) the Cl⁻ content also decreases, but the glycine content moderately increases. This is in consonance with the data [7] that glycine is coordinated to Cu(II), while Cl⁻ anions to Cu(I). From these results one may infer that the Cu(II) reduction takes place when the chloroligands are bound in the Cu(II) coordination sphere. The entrance of chloride ions into the Cu(II) coordination sphere is indicated by the colour change of the starting solution from blue to green, before the black-green copper(I)—copper(II) complexes crystallize from the solution. The prepared complexes, the composition of which fits best the formula Cu₂Cl₃·2(gly) (samples *II* and *VI*) or Cu₃Cl₅·4(gly) (sample *III*), exhibit in their electronic spectra in the visible and close ultraviolet region two absorption bands with maxima at 740 and 365 nm. The same character of electronic spectra was observed with other copper(I)—copper(II) complexes, too [9].

A series of experiments summarized in Table 1 were carried out to ascertain the conditions of Cu(II) to Cu(I) reduction in the presence of glycine. Effects of anions,

Table 2

Composition of solutions and qualitative characteristics of the prepared compounds

Compound	Composition of the starting solution			H ₂ O cm ³	Temperature of concentration °C	Appearance of products
	Cu(II) salt mol	Ligand mol	Acid mol			
<i>I</i>	0.05 CuCl ₂	0.1 gly	0.2 HCl	24	22	Brown-green precipitate
<i>II</i>	Filtrate from the system <i>I</i>					Glossy black-green crystals
<i>III</i>	0.05 CuCl ₂	0.1 gly	0.2 HCl	25	90	Glossy black-green crystals
<i>IV</i>	0.05 CuCl ₂	0.1 gly	—	25	38	Blue crystals
<i>V</i>	0.005 CuCl ₂	0.01 gly	0.2 H ₂ SO ₄	15	90	Mixture of black and blue crystals
<i>VI</i>	0.05 CuCl ₂	0.1 gly	0.2 HClO ₄	25	90	Glossy black-green crystals
<i>VII</i>	0.01 CuSO ₄	0.02 gly	0.2 HCl	15	90	Mixture of black and blue crystals
<i>VIII</i>	0.01 Cu(ClO ₄) ₂	0.02 gly	0.2 HCl	15	90	Mixture of black and blue crystals
<i>IX</i>	0.01 CuSO ₄	0.02 gly	0.2 H ₂ SO ₄	15	90	Blue-green precipitate
<i>X</i>	0.01 Cu(ClO ₄) ₂	0.02 gly	0.2 HClO ₄	15	90	Blue needlelike crystals
<i>XI</i>	0.005 CuCl ₂	0.01 α-ala	0.2 HCl	20	90	Dark green thick solution and glossy black crystals
<i>XII</i>	0.005 CuCl ₂	0.02 β-ala	0.2 HCl	20	90	Light green crystals
<i>XIII</i>	0.01 CuCl ₂	0.02 eta	0.2 HCl	20	90	Light green crystals
<i>XIV</i>	0.02 CuCl ₂	—	0.2 CH ₃ COOH	10	38	Blue-green crystals

Abbreviations: gly = glycine; α-, β-ala = α-, β-alanine; eta = ethanolamine.

acidity of the medium, position of the amino group in regard to the carboxyl group, the presence of the amino or carboxyl groups, and the role of temperature were investigated.

As we have already stated, the copper(I)—copper(II) complexes were obtained when the system contained in addition to CuCl_2 and glycine also hydrochloric acid (Table 2, systems *I*, *II*, and *III*). In the case when strongly acidic solutions of Cu(II) and glycine contained, besides chlorides, also sulfate or perchlorate ions added to the system either in the form of the corresponding acids (systems *V* and *VI*) or as cupric salts (systems *VII* and *VIII*), mixtures of compounds containing also copper (I)—copper(II) complexes were formed predominantly. Interesting is the comparison of systems *VI* and *VIII* which contain both chlorides and perchlorates. The solid reaction products varied according to the way how the respective anions were added to the system. When the system was prepared from cupric chloride and perchloric acid, only the crystals of copper(I)—copper(II) complex were formed. The system prepared from cupric perchlorate and hydrochloric acid afforded a mixture of black and blue crystals. Formation of copper(I)—copper(II) complexes was not observed in systems containing sulfate or perchlorate anions in the absence of chlorides (systems *IX*, *X*).

Copper(I)—copper(II) complexes were not formed in the system containing CuCl_2 and glycine which was not acidified (system *IV*). Concentration of the solution led to crystallization of a blue compound free of Cu(I) of a composition close to $\text{Cu}_3\text{Cl}_4 \cdot 4(\text{gly}) \cdot 5\text{H}_2\text{O}$. Only one absorption band having the maximum at 740 nm occurs in its electronic spectrum recorded in the visible and close ultraviolet region.

From the results described above, a conclusion can be drawn that the reduction of Cu(II) to Cu(I) in the presence of glycine is conditioned by the presence of chloride ions and by strong acidity of the medium. In connection with this fact it became of interest to find out to what extent is the Cu(II) reduction dependent upon the presence of the carboxyl and amino groups in glycine, and their relative position in the ligand molecule. We examined therefore the systems in which glycine was replaced by α -alanine, β -alanine, ethanolamine or acetic acid. It was found that Cu(II) to Cu(I) reduction takes place only in the system with α -alanine. The Cu(II) reduction did not proceed in the presence of acetic acid (system *XIV*), which means that the carboxyl group alone is insufficient to induce the Cu(II) reduction. The experiments with β -alanine (system *XII*) showed that the reduction does not occur too when the carboxyl and amino groups are present in the ligand molecule in other than α position. It can be concluded that the amino group requires an α -linked carboxyl group because the Cu(II) reduction was also not observed in the presence of ethanolamine (system *XIII*). Thus, in addition to chlorides and strong acidity of the aqueous medium, the presence of an α -amino acid appears to be a prerequisite for the Cu(II) to Cu(I) reduction. If these

conditions are not fulfilled Cu(II) reduction does not proceed even at increased temperatures (Table 2).

The composition of the coordination sphere of the complexes, which undergo redox changes in the studied systems, will be a subject of our further work. In analogy with the literature data [1, 2] we assume that the Cu(II) reduction is conditioned by various σ -donating or π -accepting properties of ligands bound in the Cu(II) heterogeneous coordination sphere. In this connection it is of interest to note that copper(I)—copper(II) complexes are also formed in the systems containing chlorides or bromides and glyoxanil(1)-phenylhydrazone [10]. Reduction of Cu(II) to Cu(I) in these complexes can also be regarded as a consequence of a mutual influence of halides and glyoxanil(1)-phenylhydrazone, which has a disposition for binding to the central atom with a π -dative bond. The composition of complexes of Cu(II) with glyoxanil(1)-phenylhydrazone was variable to a certain degree, similarly as that of Cu(II)—glycine complexes reported here. This fact can be ascribed to a "competition" among the simultaneous complex-forming, chelating, and redox reactions [10]. A similar consideration may account for the effects of the reaction conditions (temperature, solution concentration, content of chloride ions) on product composition observed in the present work.

Comparison of our results with others [6, 11] points out that a suitable combination of ligands in the coordination sphere of Cu(II) complexes may result in a spontaneous (thermic) redox change comparable to the effect of irradiation on complexes which contain only one type of ligands in the coordination sphere [6]. Additional ligand entering the coordination sphere operates there as a "promoter" of the redox reaction alike the u.v. radiation in the case of the Cu(gly)₂ complex.

References

1. Gažo, J., *Chem. Zvesti* 15, 20 (1961).
2. Gažo, J., *Novel in Coordination Chemistry. Section Lectures of the XIIIth ICC, Cracow—Zakopane, 1970*, p. 293. Państwowe Wydawnictwo Naukowe, Wrocław—Warsaw, 1974.
3. Baker, J., Nyburg, S. C., and Szymanski, J. T., *Inorg. Chem.* 10, 138 (1971).
4. Boos, G. A., Solovyeva, T. F., and Zakharov, A. V., *Zh. Neorg. Khim.* 24, 1914 (1979).
5. Nakasuka, N., Martin, R. P., and Scharff, J. P., *Bull. Soc. Chim. Fr.* 1975, 1973.
6. Ilyukevich, L. A., Shagisultanova, T. A., and Sidorova, I. T., *Khimiya Vysokikh Energii* 3, 364 (1969).
7. Glowiak, T. and Kozłowski, H., *Inorg. Chim. Acta* 46, 65 (1980).
8. Gažo, J. and Šramko, T., *Chem. Zvesti* 11, 633 (1957).
9. Kelló, E., Vrábek, V., Melnik, M., Dunaj-Jurčo, M., and Garaj, J., *Z. Anorg. Allg. Chem.* 417, 229 (1975).
10. Chiswell, B. and O'Reilly, E. J., *Inorg. Chim. Acta* 35, 141 (1979).
11. Sýkora, J., Šima, J., Valigura, D., Horváth, E., and Gažo, J., *Proceedings of the IIIrd SOPTROCC*, p. 112. Mogilany—Cracow, May, 1980.