

KINETICS AND EQUILIBRIA IN THE SYSTEM TRANS-BIS-(THIOSULPHATO)-BIS(ETHYLENE-DIAMINE)COBALT(III)-TRANS THIOSULPHATO-AQUA-BIS (ETHYLENEDIAMINE) COBALT(III)

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The aqua-thiosulphato-bis(ethylenediamine) cobalt(III) complex $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH}_2)]^+$ has been prepared in solution by normal hydrolysis and/or stoichiometric oxidation of trans-bis(thiosulphato) bis(ethylenediamine) cobalt(III) complex with iodine. The product of oxidation has been isolated by ion-exchange chromatography and has been characterized on the basis of its UV spectroscopic parameters and its substitution chemistry. The acidity constant of the aqua-product has been measured using spectrophotometric titration method and was found to be 7.383 ± 0.03 .

Key words: Preparation and characterization of aqua-thiosulphato bis(ethylenediamine) cobalt (III) complex.

INTRODUCTION

The anion complex $\text{trans-}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ is known since Ray and Maulik [1] isolated it as sodium salt, but very little is known about its chemistry or its derivatives.

Babaeva *et al.* [2] reported that $\text{trans-}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ does not react with sodium sulphite or nitrite in aqueous solution at room temperature, but that heating with SO_3^{2-} yielded $\text{trans-}[\text{Co}(\text{en})_2(\text{SO}_3)_2]^-$.

Recently, kinetic and competition studies of the $\text{trans-}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ with N_3^- , NCS^- , NO_2^- and CH_3CO_2^- have been reported by one of us [3] using UV-Vis and HPLC techniques.

A perusal of the literature reveals that only one brief report [4] has so far appeared on the preparation of the aqua-thiosulphato-bis(ethylenediamine) cobalt(III) complex by oxidation of $\text{trans-}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ with iodine. We describe here in detail the preparation of the aqua-complex $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH}_2)]^+$ from hydrolysis and oxidation of $\text{trans-}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$. The characterization of the aqua-complex was based upon its UV parameters and its anation reactions with different nucleophiles.

EXPERIMENTAL

G.P. grade sodium perchlorate, azide, thiocyanate, nitrite and acetate were used without purification. The complex $\text{trans-Na-}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]$ was prepared by Ray's method [1] and Cooper *et al.* [4] modification. Its visible-ultraviolet spectrum is consistent with that previously reported [5,6] for the trans isomer. The elemental

analysis of solid $\text{trans-Na}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]$ was performed by the Analytical services, department of chemistry at the Queen University of Belfast, N. Ireland (England). Anal. Calcd: C, 11.27; H, 3.78; N, 13.14; Co, 13.82; Na, 5.39; Found: C, 11.42; H, 3.71; N, 12.96; Co, 14.0; Na, 5.4. Visible-UV spectra were recorded on VSU2 spectrophotometer. Some experiments were carried out using a Perkin-Elmer 402 UV-visible spectrophotometer.

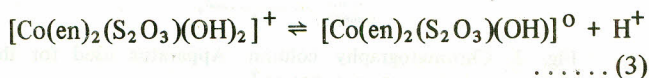
Acidity constant measurement. In order to determine the acidity constant at 25° of the aqua-complex $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH}_2)]^+$, a spectrophotometric titration was performed. The solution and titrant were maintained at $[\text{Na}^+] = 1.0 \text{ M}(\text{NaClO}_4)$. The following four buffers $\text{H}_3\text{BO}_3\text{-NaOH}$ (pH, 8-10, $\text{pK}=8.894$) [7], $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ (pH, 8.5-10.5, $\text{pK}=9.529$) [8], $\text{Na}_2\text{HPO}_4\text{-NaH}_2\text{PO}_4$ (pH, 6-8, $\text{pK}=6.34$) [8] and trimethoxy methylamine (Tris)- HClO_4 (pH, 7-9, $\text{pK}=8.25$) [9] were used with total concentration 0.01 mol.dm^{-3} . The pH values were controlled using the equation [1].

$$\text{pH} = \text{pK}(\text{buffer}) + \log[\text{salt}]/[\text{acid}] \dots \dots \dots (1)$$

for pH values higher or lower than quoted above, equation(1) is not valid and mixtures of $\text{H}_3\text{BO}_3\text{-HClO}_4$, $\text{Na}_2\text{CO}_3\text{-NaOH}$, $\text{NaHCO}_3\text{-HClO}_4$, $\text{NaH}_2\text{PO}_4\text{-HClO}_4$ and Tris-NaOH were used and pH values were checked with pH meter. The absorbancies were measured at 289 nm (Analytical wavelength) with complex concentrations lie between $(5-6) \times 10^{-5} \text{ mol. dm}^{-3}$. The acidity constant values were calculated as described by Albert and Serjeant [10] using the equation(2).

$$\log(d_A - d)/(d - d_B) = \log K_a - \log[H^+] \dots \dots \dots (2)$$

where d is the absorbancy of the solution at a given hydrogen ion concentration (H⁺), d_A and d_B are the absorbancies of the solution in fully acidic and basic form respectively, and K_a is the acidity constant for the reaction(3),



The pK_a was found to be 7.383 ± 0.03 in good agreement with the value 7.4 ± 0.1 published by Cooper *et al.* [4]. Table 1 shows the experimental observations data obtained at different pH values. The quoted pK value was obtained using the data reported in Table 1 and equation 2.

Table 1. Absorbancies at 289 nm of 5 x 10⁻⁵ M trans thio-sulphato-aqua-bis(ethylenediamine) cobalt(III) at different pH values.

pH	Buffer	NaH ₂ PO ₄ Na ₂ HPO ₄	Tris- HClO ₄	Na ₂ CO ₃ NaHCO ₃	H ₃ BO ₃ NaOH
6.0		0.571	—	—	—
6.5		0.588	—	—	—
7.0		0.611	0.560	0.634	—
7.5		0.615	0.567	—	—
8.0		0.617	0.564	0.638	0.616
8.1		—	—	0.643 ^(a)	—
8.5		—	0.650	0.662	0.681
9.0		—	0.681	0.675	0.804
9.5		—	—	0.700	0.800
10.0		—	—	0.740	0.804
11.0		0.667	0.664	0.773 ^(b)	0.800

(a) mixture of 0.1 M NaHCO₃ and 10⁻³ M HClO₄.

(b) mixture of 0.1 M Na₂CO₃ and 1.708 x 10⁻³ M NaOH.

RESULTS AND DISCUSSION

Preparation and characterization of aqua-thiosulphato-bis(ethylenediamine) cobalt(III) complex:

(A) By normal hydrolysis of trans[Co(en)₂(S₂O₃)₂]⁻. In a typical experiment, stock solutions of (2.4-5.6) x 10⁻⁵ mol.dm⁻³ trans[Co(en)₂(S₂O₃)₂]⁻ were made up at room temperature in a volumetric flask with unit ionic strength (NaClO₄). 2.5 ml of the solution was measured using a checked pipette into the cuvette of the spectrophotometer and allowed to hydrolyse at 25^o. The change in absorbance was followed without removing the cell from its compartment. The complex trans-[Co(en)₂(S₂O₃)₂]⁻ exhibits an

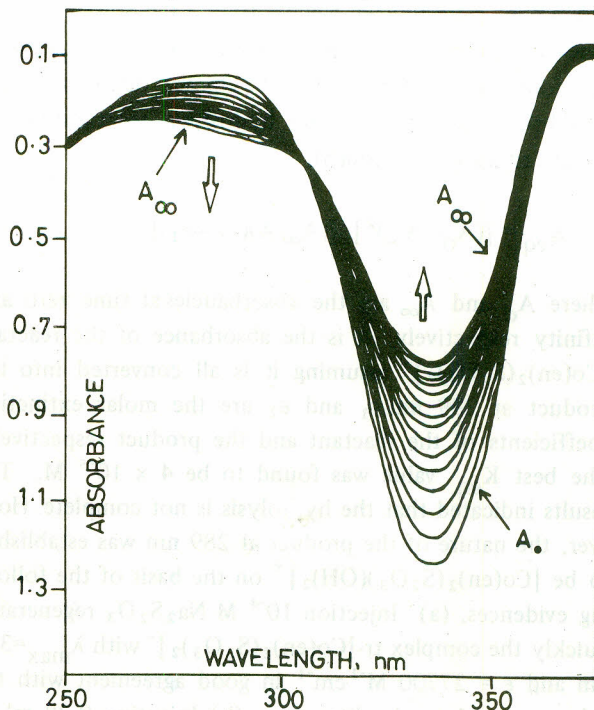
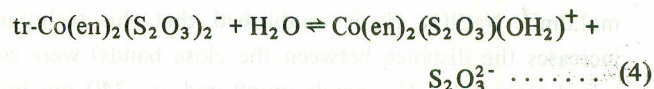


Fig. 1. The hydrolysis of 3.8 x 10⁻⁵ M trans-Na-[Co(en)₂(S₂O₃)₂] in water at 25^o.

absorption spectrum with a ligand field band at 333 nm (ε = 27700 M⁻¹ cm⁻¹). The spectral changes obtained upon hydrolysis are shown in Fig. 1. The product of hydrolysis has a peak maximum at 289 nm. The fall in the concentration with times at 333 nm was in good agreement with the concentration of the product at 289 nm indicating that one product only is formed. The spectra showed an isosbestic point at 306 nm which slightly shifted to 304 nm after ~ 100 minutes, and could be due to some side-reaction, possibly the isomerization of trans to cis-product. The rate of hydrolysis was found to be slow with half life ~ 2 hrs. and tend to an equilibrium.

The observed hydrolysis rate constants k_{hyd.} of the reaction (4)



were obtained from plotting log_e (A_t - A_{t+n}) against time t, where A_t and A_{t+n} are the absorbancies at time t and after a fixed time interval “n” respectively. The k_{hyd.} values were used to estimate A_∞(absorbance at infinity) using Guggenheim [11] equation (5),

$$A_{\infty} = [A_t - A_0 \exp(-k_{hyd.} t)] / [1 - \exp(-k_{hyd.} t)] \dots \dots \dots (5)$$

where A_t = A₀ at time t = zero. The A_∞ values for each

experiment were plotted against time, extrapolated to zero time and the real A_{∞} was obtained. The best k_{hyd} value was found to be $8.8 \times 10^{-5} \text{ s}^{-1}$. On the other hand, the equilibrium constant of the hydrolysis reaction(4) was calculated using equation(6),

$$K_{\text{eq}} = [(A_0 - A_{\infty})^2] / [(A_{\infty} - A)(\epsilon_1 - \epsilon_2)] \dots \dots \dots (6)$$

where A_0 and A_{∞} are the absorbancies at time zero and infinity respectively. A is the absorbance of the reactant $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ assuming it is all converted into the product at 289 nm. ϵ_1 and ϵ_2 are the molar extinction coefficients of the reactant and the product respectively. The best K_{eq} value was found to be $4 \times 10^{-5} \text{ M}$. The results indicated that the hydrolysis is not complete. However, the nature of the product at 289 nm was established to be $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH})_2]^+$ on the basis of the following evidences, (a) Injection $10^{-4} \text{ M Na}_2\text{S}_2\text{O}_3$ regenerated quickly the complex $\text{tr}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ with $\lambda_{\text{max}} = 333 \text{ nm}$ and $\epsilon = 27700 \text{ M}^{-1}\text{cm}^{-1}$ in good agreement with the values quoted in the literature, (b) Injection 0.28 ml of 1 M nucleophiles $\text{X}(\text{X} = \text{N}_3^-, \text{NCS}^-, \text{NO}_2^- \text{ and } \text{CH}_3\text{COO}^-)$ with final concentration 0.1 M into the product of hydrolysis yielded the derivatives $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{X})]$ very fast followed by slow formation step. This may support the conclusion that the hydrolysis product is actually mixture of $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH})_2]^+$ and $\text{trans}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$. The derivatives $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{X})]$ were identified by comparing the spectra obtained with those already published [4].

(B) By oxidation of $\text{trans}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ with iodine. The method described here is mainly as given by Deutsch's method with some modification. $0.04 \text{ mol. dm}^{-3}$ $\text{trans}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ were oxidized with $0.06 \text{ mol. dm}^{-3}$ I_2/I^- (pH = 5, HClO_4) in $\sim 2 \text{ ml}$ of water. The reaction mixture is loaded on to a sephadex sp - 25 cation exchange column (Na^+ form, $2 \times 24 \text{ cm}$) and the bands eluted with $0.05 \text{ mol. dm}^{-3}$ NaClO_4 followed by $0.25 \text{ mol. dm}^{-3}$ NaClO_4 (it is established that this technique increases the distance between the close bands) were collected separately. The bands monitored at 340 nm by a flow cell in the spectrophotometer. The behaviour of the product of oxidation toward ion-exchange resin provide an additional support for the formulation of the product as a cation species. The fractionation of the products of oxidation on the sephadex column is illustrated in Fig. 2. Four bands were observed on the cation column. B and A (green) for unreacted $\text{trans}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ was eluted quickly. Bands B (pink) and C (green) were very close to each other, but on changing the eluent concentration from 0.05 to

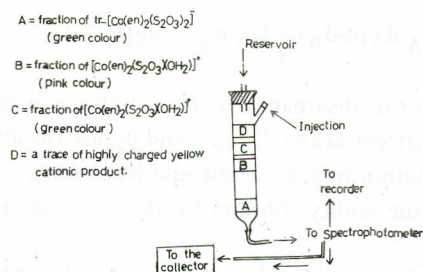


Fig. 2. Chromatography column. Apparatus used for the preparation of $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH}_2)]^+$.

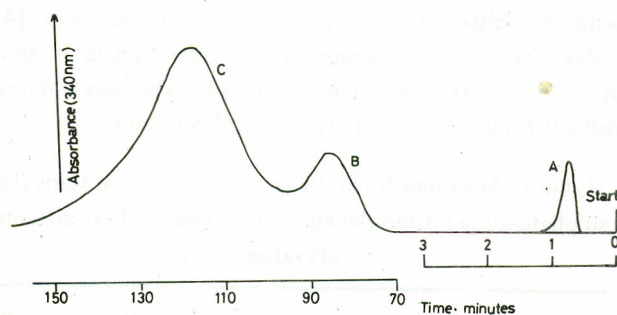


Fig. 3. Spectrophotometrically separation of the oxidation reaction products on Sephadex SP-25 cation exchange column (Na^+ form). (A) Unreacted $\text{tr}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ (green colour), (B) Product $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH}_2)]^+$ (pink colour) and (C) Product $[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH}_2)]^+$ (green colour)

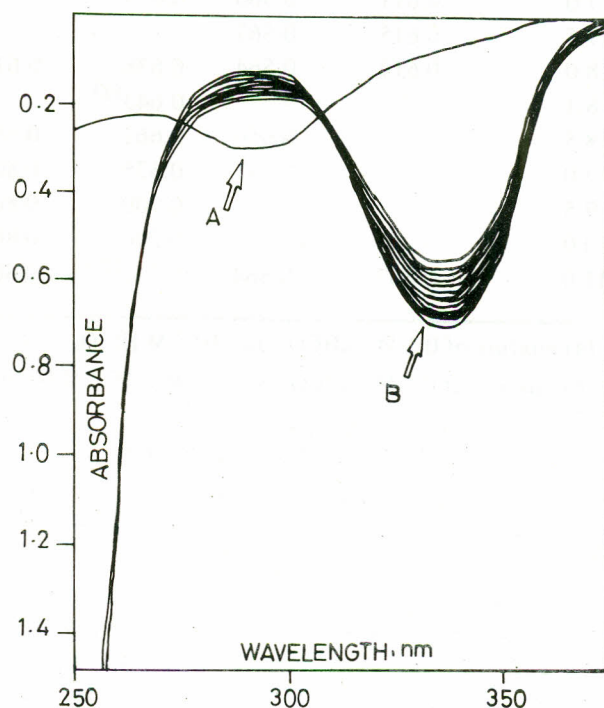


Fig. 4. (A) Absorption spectra of $2 \times 10^{-5} \text{ M} [\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH}_2)]^+$ from oxidation of $\text{tr}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ with I_3^- . (B) Absorption spectra of the product $\text{tr}[\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)_2]^-$ from reacting $2 \times 10^{-5} \text{ M} [\text{Co}(\text{en})_2(\text{S}_2\text{O}_3)(\text{OH}_2)]^+$ with $0.01 \text{ M Na}_2\text{S}_2\text{O}_3$ at 25°

0.25 mol.dm⁻³ NaClO₄, the separation occurred, and each band was collected alone. The pink band B was found to have a typical spectra as the green band C. On the other hand, the pink band B turned into green colour on standing for a few minutes after collection. An interesting observation is that the collection ratio between B and C bands is variable and depends on the initial concentration of the starting complex trans-[Co(en)₂(S₂O₃)₂]⁻. The pink band C could be unstable cis-isomer of the aqua-complex product which turned into the stable-green trans-isomer. This argument may be consistent with that observed by normal hydrolysis method, where the isosbestic point at 306 nm was shifted slightly to 304 nm after ~ 100 minutes. The fourth band (yellow) was found to be for traces of highly positive charged molecules and it takes a very long time (24-48 hrs.) to elute from the column. Fig. 3 gives a typical example of the elution order for the three bands A, B and C. At the end of the run, band B was added to band C (both have similar spectra and extinction), and the concentration calculated allowing for dilution. The nature of the solution was investigated by recording its spectrum. It was found that the ligand field band of the original species ($\lambda_{\max} = 333$ nm) vanished completely and a new band appeared at 289 nm. Injection 0.01 mol.dm⁻³ Na₂S₂O₃ to that solution produced spectra and molar extinction coefficient in good agreement with that of starting complex trans-[Co(en)₂(S₂O₃)₂]⁻ which confirms the presence of the Co(III)-(en)₂ moiety in the new product. On the other hand, anation experiments were carried out by injection N₃⁻, NCS⁻, NO₂⁻ and CH₃COO⁻ as substituting nucleophiles. The spectra and the molar extinctions of the product [Co(en)₂(S₂O₃)(nucl.)] were in agreement with those reported [3] for reacting trans-[Co(en)₂(S₂O₃)₂]⁻ with the nucleophiles referred to above. The visible-UV spectroscopic parameters and the molar extinction coefficients of solutions of [Co(en)₂(S₂O₃)(nucl.)] complexes are given in Table 2. All the complexes exhibit an intense absorption band in the 282-292 region of the UV spectrum. This band is diagnostic for the Co(III)-S bond [12,13] and has been assigned as a ligand to metal charge transfer arising from sulphur to cobalt. Attempts to isolate solid salt of the [Co(en)₂(S₂O₃)(OH)₂]⁺ were unsuccessful. The volumes of the collected B and C bands were reduced to a very small volume and were found to have the character of aqua-complex. But on drying, solid material was formed with different colour and unsatisfactory microanalysis. Anal: Calcd: for solid [Co(en)₂(S₂O₃)(OH)₂] ClO₄; C, 11.76, N; 13.71, H, 4.44 %. Found: C, 0.12, N, 0.0, H, 2.59 %. Moreover, the spectrum showed the main band missing at 289 nm. This may be due to the

Table 2. Visible-UV spectrophotometric parameters^(a) for solutions of [Co(en)₂(S₂O₃)(nucl.)] complexes from reacting [Co(en)₂(S₂O₃)(OH)₂] with nucl. = N₃⁻, S₂O₃²⁻, NO₂⁻, CH₃COO⁻ and OH⁻ nucleophiles.

Complex	λ_{\max} . (ϵ)	
[Co(en) ₂ (S ₂ O ₃)(OH) ₂] ⁺	289(8500)	—
[Co(en) ₂ (S ₂ O ₃) ₂] ⁻	289(2632)	333 (3 x 10 ⁴)
[Co(en) ₂ (S ₂ O ₃)(NCS)] ⁰	289(11950)	333 (3175)
[Co(en) ₂ (S ₂ O ₃)(NO ₂)] ⁰	292(18340)	333 (4570)
[Co(en) ₂ (S ₂ O ₃)(OH)] ⁰	283(14500)	—
[Co(en) ₂ (S ₂ O ₃)(N ₃)] ⁰	292(3760)	333 (17280)
[Co(en) ₂ (S ₂ O ₃)(CH ₃ COO)] ⁰	292(18230)	333 (8020)

(a) Wavelength λ in nm, molar extinction coefficients ϵ in M⁻¹ cm⁻¹.

decomposition of the complex caused by complete drying. The conclusion is that the complex [Co(en)₂(S₂O₃)(OH)₂]⁺ can only be prepared in solution by oxidation of trans-[Co(en)₂(S₂O₃)₂]⁻ with iodine necessitating additional work for preparing the complex [Co(en)₂(S₂O₃)(OH)₂]⁺ in solid form.

REFERNECES

1. P.R. Ray and S.N. Maulik; *J. Indian Chem. Soc.*, **10**, 655 (1933).
2. A. Babeva, I. Baranovskii and Yu. Kharnitonov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **8**, 307 (1963).
3. H.M.H. Abou-El-Wafa and M. Burnett; *Inorg. Chem. Acta Letters*, **86**, L 7 (1984).
4. J.N. Cooper, J.D. McCoy, M.G. Katz and E. Deutsch, *Inorg. Chem.*, **19**, 2265 (1980).
5. K. Akamatsu, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **50**, 533 (1977).
6. J. Hidaka, J. Fujita, Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **32**, 1713 (1959).
7. S.C. Chan and C.W. Fung, *J. Inorg. Nucl. Chem.*, **33**, 569 (1971).
8. W.M. Gilfillan, Ph.D. thesis, p. 129, Q.U.B. (1973).
9. S. Thompson and A.G. Sykes, *Inorg. Chem.*, **19**, 998 (1980).
10. A. Albert and E.P. Serjeant, *The Determination of Ionization Constants*, (Chapman and Hall Ltd., London, 1971), 2nd. ed., Chapter 4, pp. 44-64.
11. F. Wilkinson, *Chemical Kinetics and Reaction Mechanisms* (V.N. Reinhold, London, 1980), p. 76.
12. M.J. Heeg, R.C. Elder and E. Deutsch, *Inorg. Chem.*, **18**, 2036 (1979).
13. C.J. Weschler and E. Deutsch, *Inorg. Chem.*, **12**, 2682 (1973).