[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

Cysteine Complexes with the Cobalt(III) Ion. IV. Structure and Interrelationship of the Bis- and Tris-cysteinates of Cobalt(II) and Cobalt(III)

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The work of Schubert on the three cysteine complexes of cobalt(II) has been repeated and confirmed, but the green complex of cobalt to cysteine ratio 1:1 was shown to be unstable in presence of oxygen. Coördination *via* the amino and sulfhydryl groups of cysteine in the bis- and tris-complexes of cobalt(II) was established by comparison with spectral and oxidation behavior of the corresponding 2-mercaptoethylamine complexes.

Complexes of cysteine with the cobalt(II) ion were first studied by Michaelis and co-workers[3] who showed that, at *p*H 7–8 in entire absence of oxygen, a cobalt(II) complex formed that was "usually slightly olive-green" but became pink in presence of a large excess of cysteine. The complex was oxidized very rapidly by oxygen, organic dyes, and by ferricyanide to an intensely dark-brown complex of cobalt(III) in which, according to Michaelis, the cobalt to cysteine ratio was 1:3. Kendall and Holst[4] later carried out a quantitative study of the oxidation of the cobalt(II) complex and concluded the cobalt to cysteine ratio was 1:2.

Little progress was made in this subject until Schubert[5] described the isolation in the solid state of three cysteine complexes of cobalt(II), prepared in absence of oxygen, in which the cobalt to cysteine ratios were 1:1 (A), 1:2 (B) and 1:3 (C). Complex A, designated cobaltous cobalto bis-cysteinate by Schubert, was grass-green in color, insoluble in water, and was precipitated by mixing one mole of cysteine hydrochloride with one mole of cobalt(II) chloride and one mole of potassium hydroxide, the resultant *p*H being 7 to 8. Addition of one mole of potassium hydroxide gave soluble green complex B and 0.5 mole of cobalt(II) hydroxide. Complex C, blue-violet, was made from one mole of cobalt(II) ion and an excess of alkaline potassium cysteinate.

This paper describes work verifying the original preparative techniques of Schubert together with the results of a spectrophotometric study of the bis-cysteinate and bis-(2-mercaptoethylamine) chelates with cobalt(II) to establish the nature of coordination in the complexes of cobalt(II) with cysteine.

Results and Discussion

Using the apparatus previously described[6] for the preparation of complexes in absence of oxygen the three complexes reported by Schubert were prepared. The grass-green complex A very rapidly turned brown on exposure to air. This was due to the formation of cobalt(III) bis-cysteinate which was identified in solution spectrophotometrically when the green complex was stirred with water. This observation is not in agreement with the statement of Schubert that the green complex "is so stable that it can even be prepared in the presence of air." As this complex was insoluble in water and in common organic solvents no measurement of its absorption spectrum was possible.

For spectrophotometric determinations the deep-green potassium salts of cobalt(II) bis-cysteinate and bis-(2-mercaptoethylamine) were prepared in solution, no attempt being made to isolate the solid complexes as this was found always to lead to contamination with oxidation products. The spectra, which were essentially identical, were determined in the range 325–700 mμ, absorption maxima occurring at 350 and 445 μu. The values for the extinction coefficients are 1.86×10^3 and 0.59×10^3, respectively. Introduction of oxygen resulted in immediate formation of the corresponding brown cobalt(III) bis-complexes, which were identified by their spectra.[6]

Attempts to prepare the potassium salts of cobalt(II) tris-cysteinate and tris-(2-mercaptoethylamine) by reaction of cobalt(II) ion with excess potassium cysteinate above *p*H 9 resulted in solutions ranging in color from pink to blue-violet. No attempts were made, therefore, to determine the spectra of these solutions. In all cases introduction of oxygen immediately resulted in the formation of the green tris-complexes of cobalt(III) in which, it was shown elsewhere,[6,7] sulfhydryl and amino coordination occur.

The spectral data on the bis-chelates of cysteine and 2-mercaptoethylamine with cobalt(II) ion and the production of cobalt(III) complexes of known structure from both bis- and tris-complexes of cobalt(II) on exposure to oxygen lead to the conclusion that coördination in the bis- and tris-cysteinates of cobalt(II) occurs through the amino and sulfhydryl groups of cysteine.

Experimental

Apparatus and Materials.—Absorption spectra were determined using a Beckman spectrophotometer, model DU, and Thunberg tubes as described elsewhere.[6] Cysteine hydrochloride and 2-mercaptoethylamine of C.P. grade were obtained from Eastman Organic Chemicals, Rochester, New York. Cobalt(II) chloride hexahydrate was supplied by the J. T. Baker Chemical Co., Phillipsburg, New Jersey. Analytical procedures for determination of sulfhydryl group and cobalt are described elsewhere.[8] Cobalt(II) complexes were prepared in complete absence of oxygen in the apparatus previously described.[6]

Cobaltous Cobalto Bis-cysteinate.—This complex was prepared by the method of Schubert. On exposure to air the dry grass-green crystals immediately turned brown.

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(1) Abstracted in part from the Ph.D. thesis of Roy G. Neville, deposited in the University of Oregon library, September, 1954.

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(3) L. Michaelis and E. S. G. Barron, *J. Biol. Chem.*, **83**, 191 (1929); L. Michaelis and S. Yamaguchi, *ibid.*, **83**, 367 (1929); L. Michaelis, *ibid.*, **84**, 777 (1929).

(4) E. C. Kendall and J. E. Holst, *ibid.*, **91**, 435 (1931).

(5) M. P. Schubert, THIS JOURNAL, **53**, 3851 (1931); **55**, 3336 (1933).

(6) R. G. Neville and G. Gorin, *ibid.*, **78**, 4893 (1956).

(7) R. G. Neville and G. Gorin, *ibid.*, **78**, 5511 (1956).

(8) R. G. Neville and G. Gorin, *ibid.*, **78**, 4891 (1956).

Stirring 1.0 g. of the crystals in water gave a dark-brown solution which possessed absorption maxima at 280, 350 and 440 mμ, characteristic of cobalt(III) bis-cysteinate.[6]

Bis-chelates of Cysteine and 2-Mercaptoethylamine with Cobalt(II).—The deep emerald-green potassium salt of cobalt(II) bis-cysteinate was prepared in solution by mixing 2.13 ml. of 0.10 M cysteine (94%–SH) with 1.00 ml. of 0.10 M cobalt(II) chloride at *p*H 9.0 (in potassium hydroxide). Using 2-mercaptoethylamine the corresponding bis-complex was obtained.

Absorption spectra were determined using 1×10^{-3} M solutions. Introduction of traces of oxygen resulted in immediate formation of dark-brown bis-complexes of cobalt(III).

Tris-chelates of Cysteine and 2-Mercaptoethylamine with Cobalt(II).—Solutions of potassium cobalt(II) tris-cysteinate were prepared by treating 1.00 ml. of 0.10 M cobalt(II) chloride with 5.00 ml. of 0.10 M cysteine in potassium hydroxide at *p*H 11.0. These solutions ranged in color from deep-pink to blue-violet, immediately becoming deep-green on exposure to oxygen. The complexes of 2-mercaptoethylamine were similarly prepared, and behaved in the same manner on oxidation. For spectrophotometric use the oxygenated solutions were diluted to 5×10^{-4} M.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Isomeric Dithiocyanatotetraaquochromium(III) Ions; their Separation, Spectra and Relative Stabilities[1,2]

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The previously unresolved geometrical isomers of dithiocyanatotetraaquochromium(III) ion have been separated by ion-exchange methods. It is suggested that the more easily eluted isomer is that with the *trans* configuration since the *trans* isomers of other cationic octahedral complexes are invariably more easily eluted than the *cis* isomers. The spectra of the separated isomers are reported; these spectra do not provide a substantial test of the predictions of the crystal-field theory because of the proximity of water and thiocyanate ion in the *spectrochemical series.* At equilibrium in aqueous solution at 95°, the value of $K = (trans)/(cis)$ is approximately 0.5.

The number of possible isomers of dithiocyanatotetraaquochromium(III) ion is six if the thiocyanate ion can be bonded to chromium at either the sulfur end or the nitrogen end. A recent X-ray crystallographic study on $NH_4(Cr(NCS)_4(NH_3)_2)\cdot{}^2/_3H_2O$ indicates that in this compound the nitrogen end of the thiocyanate ion is bonded to chromium(III).[3] If one assumes the same kind of bonding in $Cr(NCS)_2(OH_2)_4^+$, only two isomers, a *cis* and a *trans* form, are possible. Previous studies on chromium(III) thiocyanate complexes have not, however, demonstrated the existence of each of these two isomers in equilibrated solutions containing chromium(III) and thiocyanate.[4-6] The ion-exchange method, which has proved to be successful in separating inert isomeric cationic octahedral complex ions,[7] has been utilized in the present study. The separation of the isomers has been accomplished; this has allowed the evaluation of the equilibrium constant for the isomerization reaction and also the establishment of the spectra of the separated isomers. These spectra are of interest both as a means of identifying the species and also because of the current flurry of activity in the interpretation of the spectra of transition metal complexes.

Experimental Methods

Reagents.—Chromium(III) perchlorate was prepared by the reduction of reagent grade chromium(VI) oxide with formic acid in perchloric acid solution followed by recrystallization of the product. All other chemicals were reagent grade and were used without further purification. The cation resin used was Dowex-50 W which had been twice taken through a 24-hour treatment with concentrated sodium hydroxide followed by a 24 hour treatment with concentrated hydrochloric acid. The resin was used in the hydrogen ion form. The chromium(III)-thiocyanate complexes were formed by heating relatively concentrated solutions containing chromium(III) perchlorate (0.8 to 1.1 M) and approximately 3 moles of potassium thiocyanate per gram atom of chromium(III) for a time long enough for the establishment of equilibrium. The precipitated potassium perchlorate was removed from the mixture after first cooling to 0°. The chromium(III) species formed at the elevated temperature persist at room temperature for long periods of time because of the inertness of these species.[4-6]

Equipment Used.—Both a Beckman model DU spectrophotometer and a Cary recording spectrophotometer were used in the course of this work. Ion-exchange columns of both 120 and 240 cm. length were used. The column cross-section area was 0.64 cm.^{2}. In general, the eluent flow rate was approximately 50 ml. per hour. The eluent was collected in 12.5-ml. portions using an automatic fraction collector which was a modification of one built by Mr. Patrick Gallagher. In general, a successful ion-exchange experiment lasted approximately 20 hours, 2 hours being required to put the complex ions on the column and 18 hours being required to carry out the elution.

Experimental Results

Ion-exchange Separation of the Isomers.—After preliminary measurements had demonstrated the feasibility of separating the isomeric dithiocyanatotetraaquochromium(III) ions, five column experiments were performed. The elution curve obtained in one of these experiments is presented in Fig. 1. The relative amounts of thiocyanate and chromium in the solutions coming off in *each of the two peak portions* was found by analysis[5,6] to be

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[2] Supported in part by grants from the U. S. Atomic Energy Commission and the Research Committee of the Graduate School, University of Wisconsin.

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