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 pH 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 pH 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.

Acknowledgments.—Thanks are due to the Research Corporation for their financial support.

EUGENE, OREGON

[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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RECEIVED OCTOBER 4, 1956

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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[1] Taken in part from the B.S. Thesis of Jon T. Hougen, 1956.

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

[3] Y. Saito, Y. Takeuchi and R. Pepinsky, *Z. Krist.*, **106**, 476 (1955).

[4] N. Bjerrum, *Z. anorg. allgem. Chem.*, **118**, 131 (1921); **119**, 39, 51, 179 (1921).

[5] E. L. King and E. B. Dismukes, THIS JOURNAL, **74**, 1674 (1952).

[6] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

[7] E. L. King and R. R. Walters, THIS JOURNAL, **74**, 4471 (1952); M. Mori, M. Shibata and J. Azami, *J. Chem. Soc. Japan*, **76**, 1003 (1955).

2.00 ± 0.01 to 1.00; both species are dithiocyanatochromium(III) ions and presumably chromium(III) has coördination number 6 in both species. Thus these species are isomeric ions with the formula $Cr(NCS)_2(OH_2)_4^+$. It is assumed on the basis of the observations on systems of isomeric cationic octahedral complexes with established configurations[7,8] that the more easily eluted isomer is the *trans* isomer.

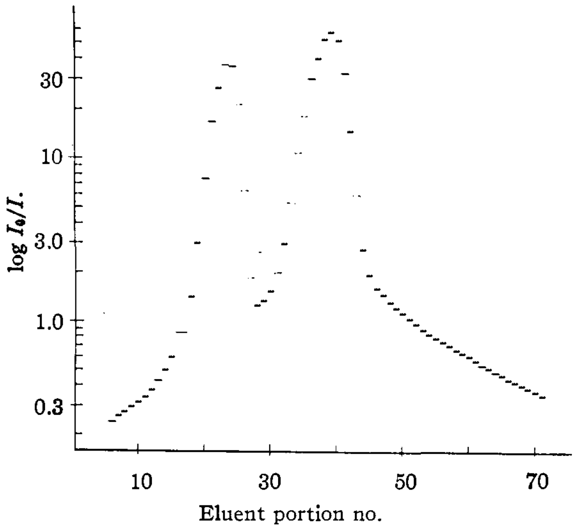

Fig. 1.—Elution curve for experiment in which ~11.5 mmoles of dithiocyanatotetraaquochromium(III) complex was eluted with 0.10 *M* $HClO_4$. Column length = 240 cm.; volume of each eluent portion = 12.5 cc.; log I_0/I measured at 270 mμ where a_{trans} = 5910 and a_{cis} = 5520; in some cases the absorbancy was measured on a diluted sample.

Judging from the amount of the resin at the top of the column into which these complexes were taken from a solution of the initial composition, 5 × 10^{-4} *M* perchloric acid and 0.02 *M* chromium(III) (primarily as ions of +1 charge), it appears that the resin is primarily in the hydrogen ion form under these conditions. In this case, the value of the partition factor *K'*, defined as the ratio of the amount of chromium in the liquid phase to the amount in the resin phase in any particular volume element,[9] should be proportional to the hydrogen ion concentration in the solution.[1] The values of *K'* determined from the linear velocity of the peak compared to the linear velocity of the eluting agent were found to be proportional to the hydrogen ion concentration: $K'_{cis}/(H^+) = 1.3 \pm 0.1$ and $K'_{trans}/(H^+) = 2.4 \pm 0.2$; the hydrogen ion concentration varied over a 10-fold range, 10^{-2} to 10^{-1} *M*. With the *K'* values determined in an initial experiment, it is relatively easy to choose, in later experiments, a concentration of hydrogen ion for the eluting agent and a column length which give both a good separation and a high concentration of the eluted species.

The Equilibrium *cis*-$Cr(NCS)_2(OH_2)_4^+ \rightleftarrows$ *trans*-$Cr(NCS)_2(OH_2)_4^+$.—The ion-exchange method of separation allows the evaluation of the relative amounts of the two isomers in an equilibrium mixture. Two such mixtures, both saturated with potassium perchlorate, were studied: sample A had the composition, 0.79 *M* chromium(III) thiocyanate–0.20 *M* potassium thiocyanate; this was heated on a steam-bath for 15 hours. Sample B also had ~3.2 moles of thiocyanate per mole chromium(III) and was approximately 1.5 times as concentrated as A and was heated at 95° for over 36 hours. Four of the ion-exchange runs were performed using mixture A with an average $K = (trans)/(cis) = 0.5_8$; the values ranged from 0.49 to 0.55. One ion-exchange run was made with sample B (the experiment pictured in Fig. 1); this gave a value of $K = 0.48$.

Thus the *cis* isomer is slightly more stable under the equilibration conditions; a *K* value of 0.50 at 370°K. corresponds to $\Delta F° = 0.5_8$ kcal. if the activity coefficient ratio is assumed to be unity. Since a reasonable estimate of a value of $|\Delta S°|$ is at most a few entropy units, the value of $|\Delta H°|$ must be less than 2 kcal. and thus a change of temperature of 20° would change *K* by only ~17%.

The Spectra of the Complex Ions.—The spectrum of no single portion of the eluent from the usual ion-exchange run can be presented as the spectrum of the pure *cis* or the pure *trans* isomer. The rate of isomerization is large enough ($t_{1/2} \cong$ 2 weeks) that some interconversion occurs during the column run. (Aquation may also be occurring to a *very* slight extent. The monothiocyanatochromium(III) complex formed on the column *does not* contaminate the eluent, however, since this

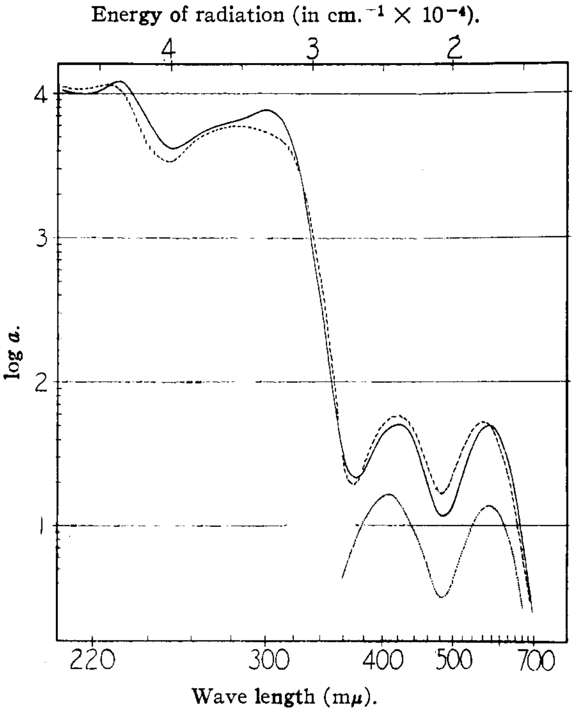

Fig. 2.—Spectra of isomeric dithiocyanatotetraaquochromium(III) ions. - - - -, *cis* isomer; ———, *trans* isomer; lowest curve, ..., $Cr(OH_2)_6^{+++}$.

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(8) P. Gallagher (unpublished work at University of Wisconsin) has demonstrated the *trans* isomers of $Co(en)_2(NO_2)_2^+$, $Co(en)_2(NCS)_2^+$, $Co(en)_2(NH_3)_2^{+++}$ and $Co(en)_2(OH_2)_2^{+++}$ are more easily eluted than the corresponding *cis* isomers.

(9) F. H. Carpenter and G. P. Hess, This Journal, **78**, 3351 (1956).

ion of charge +2 is not eluted by 0.1 *M* perchloric acid.[5]) In an effort to establish correctly the absorbancy indices for the *trans* isomer, six experiments of the breakthrough type were performed. In four of these, portions of *trans* isomer (with a trace of *cis* isomer as contaminant) were poured through a short (~ 15 cm.) column; in the other two experiments, portions of solution containing ~ 75% *trans* isomer and ~ 25% *cis* isomer were used. Thirteen portions of the solution which came through initially were examined at 270 and 300 mμ where the relative absorbancies of the two isomers are rather different. The average value of A_{300}/A_{270} on ten of these portions was 1.31 ± 0.02.[10] Since the duration of these experiments was short enough that an insignificant amount of isomerization occurred and since the same result was obtained in an experiment in which 25% *cis* isomer was present, it will be assumed that the value $A_{300}/A_{270} = 1.31$ is characteristic of the *trans* isomer. The value of A_{300}/A_{270} for portions under the second peak in a typical ion-exchange run is 0.96. With this as the first approximation of the value of A_{300}/A_{270} characteristic of the *cis* complex, it can be estimated that the material coming off in the central part of the first elution peak with a value of $A_{300}/A_{270} = 1.30$ is contaminated to an extent of approximately 3% with the less easily eluted *cis* isomer. If it is assumed that the second elution peak is contaminated with 3% of the more easily eluted *trans* isomer, the value 0.95 is calculated to be the correct value of A_{300}/A_{270} for the *cis* isomer.

In Fig. 2 are presented the spectra of the two isomeric complexes. Certain features of these curves are of interest from a theoretical point of view. The two absorption bands in the visible region of the spectrum arise from transitions involving the d electrons of the chromium(III) atom and, presumably, can be explained by the application of crystal field theory to the complex.[11] This theory predicts a splitting of the lower energy transition which is not observed. This is due, no doubt, to the close similarity of water and thiocyanate ion with regard to their positions in a "spectrochemical" series.[12] It is observed, however, that the *cis* complexes with no center of symmetry has a slightly greater absorbancy as expected.[13]

(10) Three of the portions did not come within reasonable limits of this average. Two of these deviating portions were from an experiment in which relatively pure *trans* isomer was used and the other was from an experiment on the 75–25% mixture.

(11) C. J. Ballhausen and C. K. Jorgensen, *Kgl. Danske Videnskab. Selskab, Mat. fys. Medd.*, **29**, No. 14 (1955); L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(12) Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 311, 316 (1956).

(13) F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

MADISON, WIS.

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

The Interaction of 2-Methyl-2-amino-3-butanone Oxime with Some Transition Metal Ions

BY R. KENT MURMANN

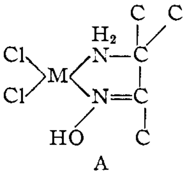
RECEIVED JULY 13, 1956

A new series of coördination compounds, formed with transition metal ions and 2-methyl-2-amino-4-butanone oxime, have been prepared. The reagent is not specific but forms stable compounds with most transition metal ions which are soluble in water and some organic solvents. With compounds having a coördination number of 4 or 6 the hydrogen bond is always formed and there is a tendency to force a *cis*-planar configuration on the molecules. The physical properties of these compounds will allow studies to be made on the effect of the hydrogen bond on stability and on the mechanism of substitution on non-ionic coördination compounds.

Introduction

It is well known that aliphatic *syn*-α-dioximes form coördination compounds with transition metal ions which contain strong hydrogen bonds[1] and that the organic ligand is often quite specific for a particular ion. Unfortunately the known compounds do not lend themselves to convenient study because of ease of hydrolysis and oxidation of the ligand and insolubility of the complexes. It was thought that a ligand capable of forming only one hydrogen bond when chelated would have more suitable properties. Thus in an effort to determine the inherent characteristics of the hydrogen bond in coördination compounds and to elucidate the mechanism of substitution reactions in non-aqueous solvents a new series of compounds have been prepared. This paper is the first of a series on this topic and presents the preparation and properties of coördination compounds of some transition metal ions with 2-methyl-2-amino-3-butanone oxime and its N-alkyl derivatives.

With metal ions having a planar configuration, Cu(II), Pd(II) and Pt(II) there are three types of compounds (ABC) which should be capable of existence. An effort has been made to produce each of these but only A and B have been isolated.



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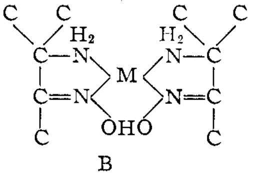

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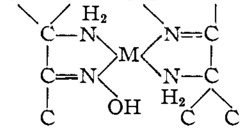

(1) L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).