[CONTRIBUTION FROM THE CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY AND THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BUFFALO]

Coördination Properties of the Thiocyanato Radical.[1] I. The Bonding of Silver and Mercury Ions by Thiocyanato Complexes of Cobalt(III) and Chromium(III)

BY W. C. WAGGENER,[2] J. ARTHUR MATTERN[3] AND G. H. CARTLEDGE[2]

RECEIVED DECEMBER 27, 1958

Silver(I) and mercury(II) ions have been found to produce color changes in solutions of *cis*- and *trans*-dithiocyanatoamminecobalt(III) salts and in the corresponding salts of chromium(III) similar to those already known for mono-thiocyanatoamminecobalt(III) salts with silver(I) ion. The nature and stability of the interaction species occurring in the solutions have been studied spectrophotometrically using the method of continuous variations. The effects of acidity and ionic strength were found to be as expected from the hydrolytic nature of the ions and the Debye–Hückel theory. The effects of light and metal ions (*viz.*, Ag(I) or Hg(II)) upon the stability of solutions of $[Co(NH_3)_5NCS](NO_3)_2$ and $[Cr(NH_3)_5NCS](NO_3)_2$, respectively, have been compared. The nature of the reaction and the identity of type established between the cobalt and chromium series of complexes are used to infer that both series have the isothiocyanato structure.

Introduction

The interaction between silver(I) ion and certain monothiocyanatoamminecobalt(III) cations in aqueous solution was discovered by Werner and Mueller in 1900.[4] They reported that addition of silver nitrate to a solution of thiocyanatopentaamminecobalt(III) nitrate caused an immediate color change from orange to yellow and that the silver ion undoubtedly was complexed with the parent cation in a rather stable type of coördination, because silver chloride was not precipitated by adding hydrochloric acid. Werner and his colleagues did subsequent work in isolating crystalline silver nitrate addition compounds, but no further studies were made upon the solutions themselves.

Difficulties were encountered in the attempt to repeat Werner's original work.[4] Pure $[Co(NH_3)_5NCS](NO_3)_2$ was prepared, but all attempts to prepare the silver addition compound having the stability ascribed to it by Werner were unsuccessful. The hydrochloric acid test always produced an immediate turbidity, followed by a slow precipitation of AgCl. Evaporation of solutions containing the parent $[Co(NH_3)_5NCS](NO_3)_2$ and $AgNO_3$ in stoichiometric proportion invariably gave a mixture of crystals, among which appeared apparently unreacted orange octahedra of $[Co(NH_3)_5NCS](NO_3)_2$.

A number of absorption measurements were made. These, too, were attended with some turbidity difficulties, due either to separation of the interaction complex or of silver thiocyanate, or of both.

While attempts to prepare a completely stable silver addition compound were in progress it was conceived that other metallic ions might interact in a manner similar to Ag ion, perhaps to form more stable and less dissociated species. Mercury(I) and (II) ions were particularly good possibilities because they, like Ag ions, form very slightly ionized thiocyanates and have pronounced tendencies to coördinate sulfur.

Qualitative tests were made with ionic salts of Tl(I), Zn(II), Cd(II), Hg(I) and (II), Cu(II) and Pb(II). Except for Hg(II) ion all were without visible effect upon the orange solution of $[Co(NH_3)_5NCS](NO_3)_2$. Mercury(II) nitrate produced the same shift toward yellow as observed for $AgNO_3$ and the color change was much more pronounced.

Crystalline, golden-yellow, Hg(II) nitrate addition salts were also isolated using $[Co(NH_3)_5NCS](NO_3)_2$. For most of the products isolated the Hg:NCS ratio was approximately 0.8:1.0; a small integral stoichiometric ratio was not obtained.

Further generalization by extending studies to the isomeric dithiocyanatoamine (*cis–trans*) complexes of tervalent cobalt was intriguing for the possible formation of rings and chains in the presence of Hg(II) ions. Extension of the interaction to thiocyanato cations of central atoms other than cobalt also was of very special interest in that it might be used to throw light upon the controversial question of orientation of the thiocyanato group coördinated in tervalent chromium complexes.

The thiocyanato group is a linear, triatomic, monoacido radical, possessing at least one unshared electron pair on each terminal atom nitrogen and sulfur. The question of which atom may be involved in bond formation in a given complex, and the possible existence of linkage isomerism attach considerable theoretical interest to study of compounds containing this group.

An experimental method which has been used to obtain information of the orientation of the coördinated thiocyanato radical in complexes of Co(III) and Cr(III) involves hydrolytic oxidation followed by examination of the resulting products Various thiocyanato complexes have been subjected to controlled, selective oxidation in solution, the resulting complexes isolated and then analyzed to determine if the thiocyanato radical had been modified, or if it had been lost completely from the parent complex. Thiocyanatoammine complexes of tervalent cobalt have been found uniformly to give the corresponding ammine complexes by hydrolytic oxidation with such agents as H_2O_2,

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(1) This paper is based in part on a thesis submitted to the Department of Chemistry of the University of Buffalo by W. C. Waggener in partial fulfillment of requirements for the degree of Doctor of Philosophy and also work done for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation. A portion of this material was presented at the 122nd National American Chemical Society Meeting in Atlantic City, N. J., September, 1952.

(2) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

(3) Chemistry Department, University of Buffalo, Buffalo, N. Y.

(4) A. Werner, *et al.*, *Z. anorg. Chem.*, **22**, 91 (1900).

TABLE I

PREPARATION OF PARENT THIOCYANATO COMPOUNDS

Compounds	Ref.		Analyses, %					
			Co	Cr	NH_3	NCS	NO_3	H_2O
$[Co(NH_3)_5NCS](NO_3)_2$	4, 9	Calcd.	18.07	...	26.11	17.80	38.02	..
		Found	18.03	...	25.95	17.72	37.85	..
		Atom ratio	1.00	...	4.98	1.00	2.00	..
$[Cr(NH_3)_5NCS](NO_3)_2$	10, 11	Calcd.	...	16.29	26.67	18.19	...	..
		Found	...	16.22	26.75	19.28	...	..
		Atom ratio	...	1.00	5.03	1.06	...	..
1,2-$[Co(en)_2(NCS)_2]NO_3$[a]	4, 12	Calcd.	16.50	...	...	32.51	...	..
		Found	16.68	...	...	32.52	...	..
		Atom ratio	1.00	...	...	1.98	...	..
1,6-$[Co(en)_2(NCS)_2]NO_3 \cdot H_2O$[a]	4, 12	Calcd.	15.70	...	...	30.95	...	4.80
		Found	15.90	...	...	31.35	...	3.59
		Atom ratio	1.00	...	...	2.00	...	0.75
1,2-$[Cr(en)_2(NCS)_2]NO_3$	13, 14, 15	Calcd.	...	14.84	...	33.15	...	..
		Found	...	14.73	...	33.43	...	..
		Atom ratio	...	1.00	...	2.03	...	..
1,6-$[Cr(en)_2(NCS)_2]NO_3 \cdot H_2O$	13. 14, 15	Calcd.	...	14.12	...	31.53	...	4.89
		Found	...	14.09	...	32.29	...	3.51
		Atom ratio	...	1.00	...	2.05	...	0.72

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[a] For metathesis HNO_3 was found superior to KNO_3.

Cl_2 or fuming HNO_3.[4-7] The degree of conversion to the ammine was dependent upon the particular complex and the nature of the oxidizing agent. On the other hand, oxidation experiments performed on a number of Cr(III) salts analogous to those of Co(III) have invariably resulted, it appears, in complete loss of the coördinated thiocyanate.[8] The uniformity of this result—the fact that no trace of an ammine derivative has been reported—has led some chemists to the opinion that the thiocyanato radical in Cr(III) complexes is coördinated through a sulfur-to-chromium bond.

Interest attaches to investigation of these interaction species as an important source for inference of orientation of the thiocyanato radical in the thiocyanatoammines of tervalent cobalt and chromium. Consequently, mono-, and *cis-* and *trans*-dithiocyanato cations of both Co(III) and Cr(III) have been included in this study.

Preparations and Analytical Methods

A summary of the preparation and analysis of the parent thiocyanato compounds used in this work is given in Table I.

Component solutions for the continuous variations experiments were prepared as follows. Solutions of $Hg(NO_3)_2$ in $HClO_4$ were prepared by dissolving a weighed sample of C.P. HgO in the calculated volumes of standardized HNO_3 and $HClO_4$. Solutions of $AgNO_3$ were prepared by dissolving a weighed sample of C.P. salt in water or acids of proper concentration. Solutions of thiocyanato complex nitrate were prepared by dissolving a weighed sample of the analyzed salt in water or acids of proper concentrations at room temperature.

Cobalt.—Cobalt was determined spectrophotometrically as the trioxalatocobalt(III) ion by the method of Cartledge and Nichols[16] after decomposition of the complexes with elimination of the coördinating groups.

The most satisfactory method found for getting the cobalt in these compounds into the divalent state involved decomposition in the dry, followed by oxidation-fusion with a mixture of ammonium persulfate and potassium pyrosulfate. Careful pyrolysis volatilized water, ammonia, and a part of the ethylenediamine present, thus minimizing foaming in the subsequent fusion. The use of potassium pyrosulfate produced a perfectly clear melt between 400 and 700°, and the use of ammonium persulfate decreased the amount of potassium pyrosulfate required for oxidation and lessened the bulk of the final melt. This melt was easily soluble in water for spectrophotometric determination.[16]

Chromium.—The complexes were decomposed in hot NaOH. Chromium was then oxidized by warm alkaline H_2O_2 and determined by standard iodometric titration.

Thiocyanate.—Thiocyanate was determined volumetrically or gravimetrically, depending upon the thiocyanato complex involved. The Volhard method was well-suited to the thiocyanatoammines since these complexes were decomposable to colorless solutions by warming with dilute alkali, in which the thiocyanate ion was quite stable. Both $AgNO_3$ and $Hg(NO_3)_2$ were tried as titrants. The end-point was slightly sharper when the latter was used, and this titrant was generally preferred. The gravimetric determination of thiocyanate as AgSCN was used in the deeply colored solutions which sometimes resulted from decomposition of thiocyanatoethylenediamines in alkali solution.

Ammine (Ammonia).—Ammonia in the pentaammine complexes was determined by distillation from NaOH solution into standard acid and titration.

Nitrate.—Nitrate was determined in the pentaammine complex salts by reduction with Zn and absorption of NH_3 as for the preceding determination.

Water.—Water was determined by weight loss in air at 100–130°.

Experimental Results

Absorption Measurements

Data were taken by using either a Bausch and Lomb Visual Spectrophotometer or a Beckman Model DU instrument. The absorption, from 950 to 220 mμ, of a typical thiocyanato cation, *e.g.*, *cis*-$[Co(en)_2(NCS)_2]NO_3$, is shown in Fig. 1, together with the change in absorption observed in the pres-

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(5) A. Werner, *Ber.*, **34**, 1733 (1901).

(6) A. Werner, *ibid.*, **40**, 774 (1907).

(7) A. Werner, *Ann.*, **386**, 39 (1912).

(8) P. Pfeiffer, *Ber.*, **37**, 4257 (1904).

(9) A. Werner, *ibid.*, **36**, 2380 (1903).

(10) W. E. Henderson and W. C. Fernelius, "Inorganic Preparations," McGraw-Hill Book Co., New York, N. Y., 1935, p. 130.

(11) A. Werner and J. v. Halban, *Ber.*, **39**, 2669 (1906).

(12) A. Werner, *Ann.*, **386**, 198 (1912).

(13) C. L. Rollinson and J. C. Bailar, "Inorganic Synthesis," Vol. II, McGraw-Hill Book Co., New York, N. Y., 1946, p. 200.

(14) P. Pfeiffer and P. Koch, *Ber.*, **37**, 4268 (1904).

(15) P. Pfeiffer, *Z. anorg. Chem.*, **29**, 122 (1901).

(16) G. H. Cartledge and P. M. Nichols, *Ind. Eng. Chem.*, *Anal. Ed.* **13**, 20 (1941).

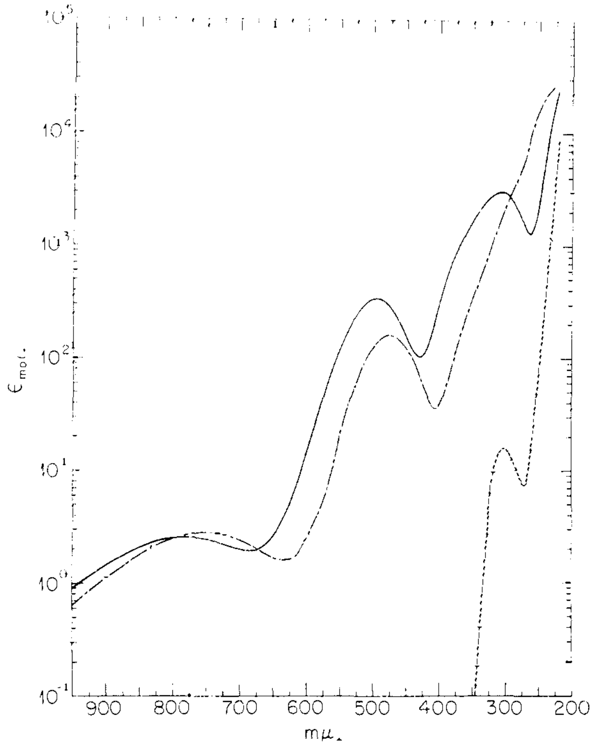

Fig. 1.—Absorption curves of *cis*-[Co(en)$_2$(NCS)$_2$]NO$_3$ and Hg(NO$_3$)$_2$ in aqueous 0.01 *M* HClO$_4$ as solvent at 24°: ———, *cis*-[Co(en)$_2$(NCS)$_2$]NO$_3$ alone; - - - -, Hg(NO$_3$)$_2$ alone; ·-·-·- *cis*-[Co(en)$_2$(NCS)$_2$]NO$_3$ and Hg(NO$_3$)$_2$ in 1:1.2 mole ratio.

ence of an excess of Hg(II) ion. The blue shift of the extinction maxima of the system in Fig. 1 is quite characteristic of the type of cation–cation interaction studied. The extinction maximum which occurs in the visible is amenable to measurement and has been used for detailed spectrophotometric studies of these systems.

The Aqueous Stability of [Cr(NH$_3$)$_5$NCS]$^{+2}$ and [Co(NH$_3$)$_5$NCS]$^{+2}$

In order to compare the chromium and cobalt systems quantitatively it was necessary to investigate to some extent the nature of the instability noted for the chromium complexes.

Aquation.—The aquation of [Cr(NH$_3$)$_5$NCS]$^{+2}$ and [Co(NH$_3$)$_5$NCS]$^{+2}$ has been studied by Adamson and Wilkins.[17] Both ions follow a first-order rate law for replacement of thiocyanate by water, the constants determined in min.$^{-1}$ being 1.17×10^{13} exp ($-24{,}900/RT$) and 0.85×10^{13} exp($-26{,}800/RT$) for the chromium and cobalt ions, respectively. From these constants at 25° the aquation is calculated to be approximately 1% per day for the Cr and much less than 0.1% per day for the Co ion.

Effect of Light.—No mention seems to have been made by previous workers of the effect of light upon [Cr(NH$_3$)$_5$NCS]$^{+2}$ though other chromium complexes are known to be sensitive.[18]

The effect of light upon the absorption spectrum of [Cr(NH$_3$)$_5$NCS](NO$_3$)$_2$ is illustrated in Fig. 2. The shifts in its absorption curve are due not simply to partial de-coördination of NCS from the pentaammine cation but also to the de-coördination of NH$_3$ from the Cr central atom. The latter effect was measured by an increase in *p*H of the solution during irradiation. The end result of irradiation of [Cr(NH$_3$)$_5$NCS]$^{+2}$ was the complete decomposition of the complex and appearance of flocculent green chromium(III) hydroxide. Thiocyanatopentaamminecobalt(III) ion under the same conditions was comparatively stable.

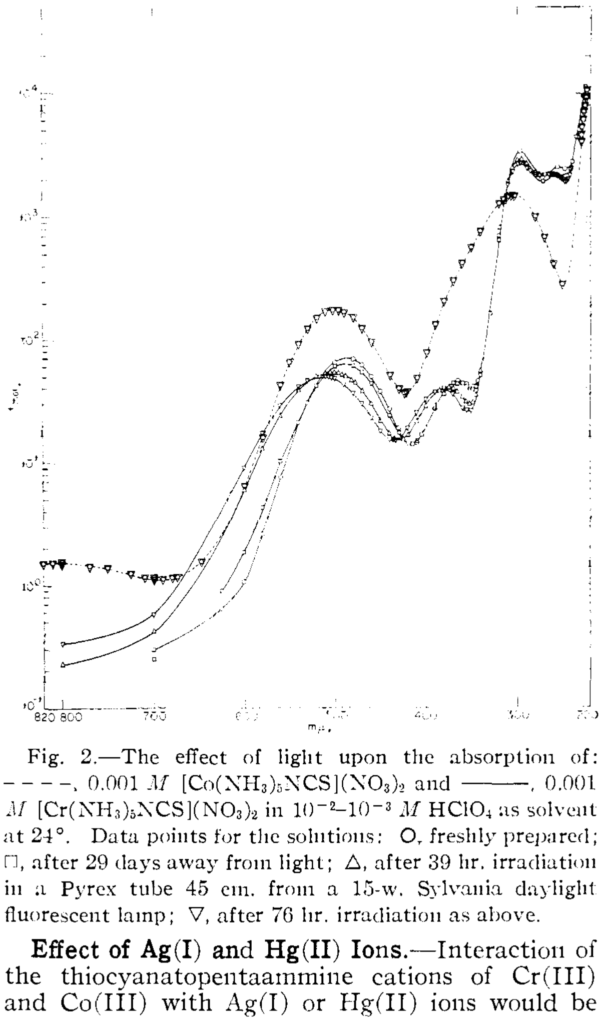

Fig. 2.—The effect of light upon the absorption of: - - - -, 0.001 *M* [Co(NH$_3$)$_5$NCS](NO$_3$)$_2$ and ———, 0.001 *M* [Cr(NH$_3$)$_5$NCS](NO$_3$)$_2$ in 10^{-2}–10^{-3} *M* HClO$_4$ as solvent at 24°. Data points for the solutions: O, freshly prepared; □, after 29 days away from light; △, after 39 hr. irradiation in a Pyrex tube 45 cm. from a 15-w. Sylvania daylight fluorescent lamp; ▽, after 76 hr. irradiation as above.

Effect of Ag(I) and Hg(II) Ions.—Interaction of the thiocyanatopentaammine cations of Cr(III) and Co(III) with Ag(I) or Hg(II) ions would be expected to increase the rate of aquation of the ammine, and this is well demonstrated in the case of the more labile chromium complex. Figure 3 shows the absorption maximum of [Cr(NH$_3$)$_5$NCS]$^{+2}$ alone and in equimolar mixture with Ag(I) and Hg(II), respectively, as a function of time. Under the conditions specified in Fig. 3 the aquation of the interaction cation follows a first-order rate plot with $t_{0.5}$ values of ~370 hr. and 1.3 hr., respectively, with Ag(I) and Hg(II) ions. The lowest-lying curve represents the experimental limit of the absorption shift with time for the [Cr(NH$_3$)$_5$NCS]$^{+2}$–Hg(II) system, and presumably corrresponds to the absorption of the completely aquated pentaammine ion.

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(17) A. W. Adamson and R. G. Wilkins, "Exchange and Aquation Studies with Thiocyanate Complexes," Tech. Rep. Office of Naval Research, Contract N6onr23809, Dept. of Chem., Univ. of So. Calif., Nov., 1953.

(18) H. J. King, *J. Chem. Soc.*, **127**, 2100 (1925).

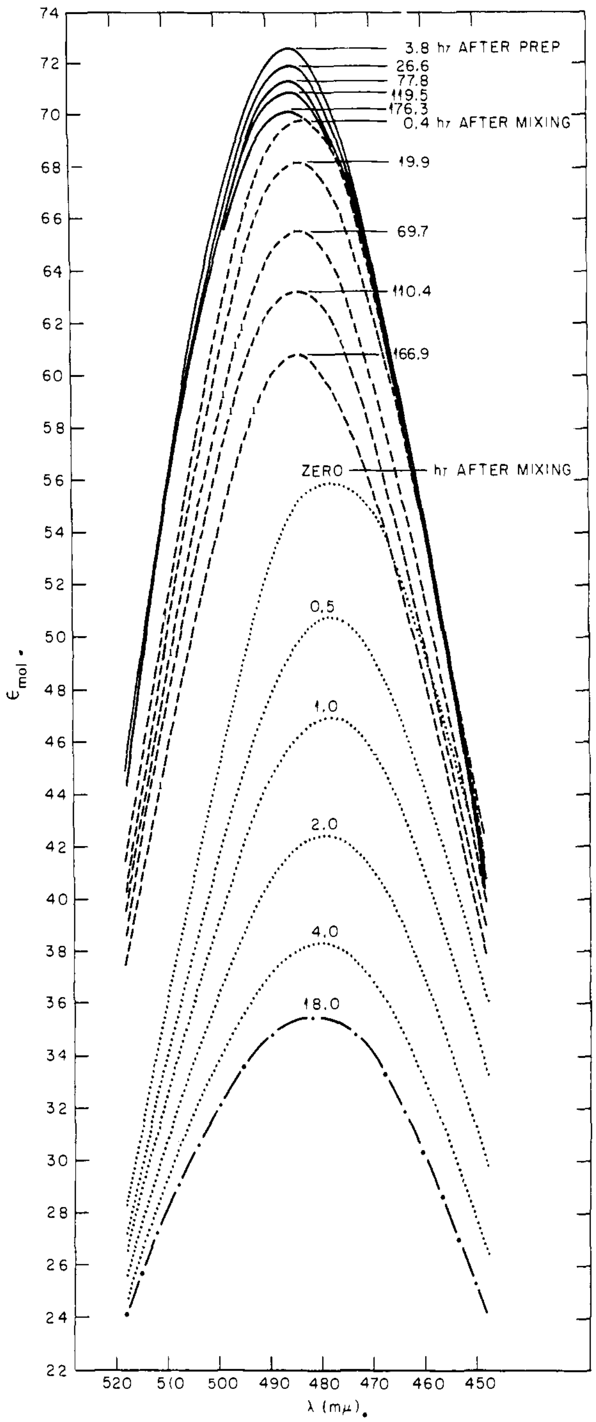

Fig. 3.—The effect or $AgNO_3$ and $Hg(NO_3)_2$, respectively, upon the absorption of $[Cr(NH_3)_5NCS](NO_3)_2$ as a function of time at 24°: ———, 0.001 *f* $[Cr(NH_3)_5NCS](NO_3)_2$ in 10^{-4} *M* $HClO_4$; - - - -, equiformal (0.001) mixture of $AgNO_3$ and $[Cr(NH_3)_5NCS](NO_3)_2$ in 10^{-4} *M* $HClO_4$; ......, equiformal (0.001) mixture of $Hg(NO_3)_2$ and $[Cr(NH_3)_5NCS](NO_3)_2$ in $HClO_4$, *p*H 1.63; -·-·-, equiformal (0.001) mixture of $Hg(NO_3)_2$ and $[Cr(NH_3)_5NCS](NO_3)_2$ in $HClO_4$, *p*H 1.63, limiting curve.

The stability of $[Co(NH_3)_5NCS]^{+2}$ in the presence of Ag(I) and Hg(II) ions, respectively, is illustrated by the series of absorption curves in Fig. 4.

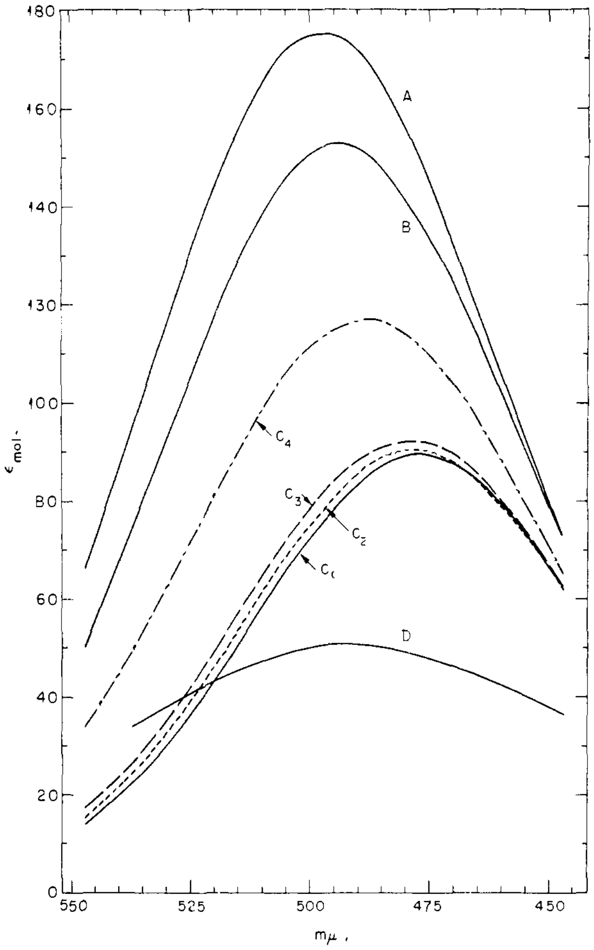

Fig. 4.—The effect of $AgNO_3$ and $Hg(NO_3)_2$, respectively, upon the absorption (447–547 mμ) of $[Co(NH_3)_5NCS](NO_3)_2$, as a function of time at 24°: (A) 0.002 *f* $[Co(NH_3)_5NCS](NO_3)_2$ alone in $HClO_4$, *p*H 2.10; (B) equiformal (0.001) mixture with $AgNO_3$ in $HClO_4$, *p*H 2.10 (no change in 4 days, (C_1 — C_4) equiformal (0.001) mixture with $Hg(NO_3)_2$ in $HClO_4$, *p*H 1.18; (D) 0.005 *f* $[Co(NH_3)_5H_2O](NO_3)_3$ alone in HNO_3, *p*H 2.00.

The temperature and the concentrations used are identical with those used for the analogous chromium system just described (see Fig. 3). The absorption of the $[Co(NH_3)_5NCS]^{+2}$–Ag(I) system in the range from 547 to 447 mμ is represented by curve B. There was no change in absorption over a period of 4 days, indicating that this system is essentially stable. A surprising series of changes was observed, however, in the absorption of the corresponding Hg(II) system during a comparable period (see curves C_1 to C_4, Fig. 4). Curve C_1 was obtained by measuring the system immediately after its preparation. Remeasurements after 8 and 22 hr. showed no change. After 68 hr. a slight increase in the absorption was noted (curve C_2). The solution was centrifuged and again remeasured after 69 hr.; curve C_3 shows that the system was in the process of a fairly rapid change at this time, with the shift in spectrum (upward and to longer wave lengths) suggesting a de-coördination of Hg(II) from the parent thiocyanatocobalt cation. Curve C_4 of Fig. 4 was obtained at 98 hr. No

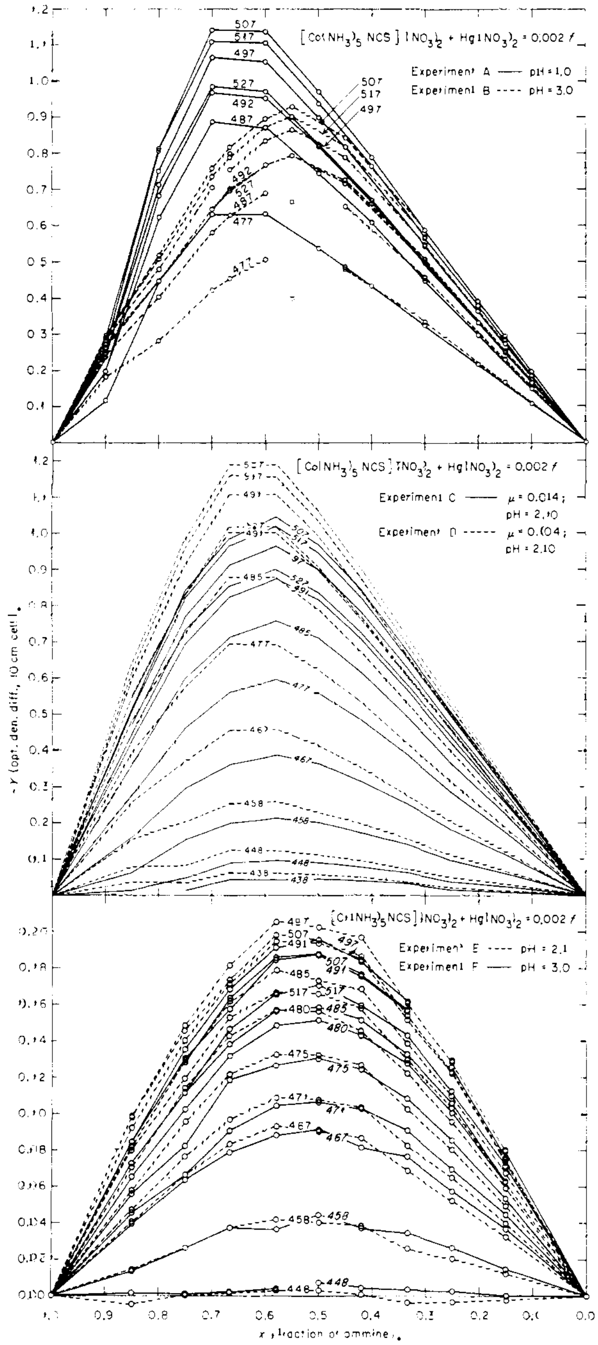

Fig. 5.—Continuous variations experiments with $[Co(NH_3)_5NCS]^{+2}$ or $[Cr(NH_3)_5NCS]^{+2}$ and Hg(II).

further change in absorption occurred in the period 98–143 hr. during which the spectrum was remeasured several times. Finally, a slight excess of NaSCN (8 *M*, 3 λ/10 ml.) was added to the system (see p. 2965) and the absorption was then found to coincide with curve A for the parent $[Co(NH_3)_5NCS]^{+2}$ ion.

The metastable nature of the system apparently is due to the hydrolytic behavior of Hg(II) ion. This would not be anticipated from the work of Hietenen and Sillén on the hydrolysis of Hg(II).[19] Their data in the same Hg(II) concentration range were explained by a mononuclear mechanism involving the formation of $HgOH^+$ and $Hg(OH)_2$ with pk_{01} and pk_{12} 3.7 and 2.6, respectively. However, their studies were conducted in the presence of higher concentrations of neutral salt ($\mu = 0.5$) which would tend to repress the hydrolytic reaction as compared to our condition of $\mu = 0.014$.

As we shall see later, further indication of the metastable nature of the $[Co(NH_3)_5NCS]^{+2}$–Hg(II) system was obtained by remeasuring the solutions of the continuous variations experiment C (Fig. 5) after heating at 50° for 9 hr. and cooling to 25°. The plot of *Y vs. x* was equally as uniform as that of experiment C. There was an average decrease in *Y* of 30% and the maximum of the *Y vs. x* plots occurred around $x = 0.5$, indicating a decrease in the effective interaction ratio from 1.4 to slightly less than 1.0.

An important adjunct to the technique of making these measurements has been the use of nitrobenzene to sequester traces of colloidal AgSCN from solution prior to spectrophotometric measurements. The very slightly ionized aqueous thiocyanatomercury(II) species $Hg(SCN)_n^{2-n}$, n = 1, 2, 3, 4 are all relatively soluble (*e.g.*, saturated $Hg(SCN)_2 = 2.2 \times 10^{-3}$ *M* at 25°)[20] and gave no trouble in the solutions studied. However, the slight solubility of AgSCN (10^{-6} *M* at 25°)[20] was a source of difficulty due to the spectrophotometric interference of colloidal AgSCN. In typical solutions such as those used in Fig. 3 the solubility product of AgSCN is exceeded as soon as aquation of the thiocyanato complex amounts to 1–2 p.p.m. A number of methods of filtration and centrifugation were tried on the solution without success before it was found that the colloidal AgSCN could be removed quite efficiently by adding 2–3 volume % of C.P. nitrobenzene, shaking the solution for several seconds, then centrifuging momentarily to separate the two phases.

Interaction Ratios of Ions in Solution

The stoichiometry of interactions between thiocyanato cations and Ag(I) or Hg(II) cations was investigated by applying the method of continuous variations to the absorption of these solutions. The data are presented in graphs of *Y* (optical density observed minus optical density calculated for no interaction) *versus x* (mole fraction of parent thiocyanato complex in mixture with $1 - x$ mole fraction of non-absorbing Ag(I) or Hg(II) cation). The interaction ratio *n* is obtained from the position of maxima or minima in the curves of *Y versus x* using the relation $n = x/(1 - x)$.

$[Co(NH_3)_5NCS](NO_3)_2$–$Hg(NO_3)_2$.—The interaction of this system is markedly dependent upon both acidity and ionic strength. Experiment A of Fig. 5 is a plot of the 0.002 *f* system $[Co(NH_3)_5NCS](NO_3)_2$–$Hg(NO_3)_2$ in 0.1 *M* $HClO_4$. For all wave lengths measured a single maximum occurs at $x = 0.67$, suggesting a 2:1 interaction between the cations. Experiment B is identical to A except that the system is in 0.001 *M* $HClO_4$ (glass electrode *p*H 3.0). Here, in comparison with

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[19] S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, **6**, 747 (1952).

[20] "Handbook of Chemistry and Physics," 13th Ed., Chemical Rubber Pub. Co., Cleveland, Ohio, 1940.

experiment A, the maximum of the curve is broadened and displaced toward $x = 0.5 (n = 1)$.

The result of experiment B is complicated by hydrolysis of the Hg(II) ion which should be negligible at the higher acidity of experiment A.[19] In 0.001 M acid the effect noted may be due to either or both of the following: the formation of a 1:1 addition species with the monohydroxymercury(II) cation or a competition between the thiocyanato cation and hydroxyl anion for mercury(II) cations.

The effect of ionic strength upon this system is apparent in experiment C and D of Fig. 5. In both experiments the acidity was constant, the measured pH of all component solutions and resultant mixtures being 2.10 ± 0.01.[21] The ionic strength of experiment C was 0.014 as calculated from the acidity and components of the 0.002 M system.

By adding 8 M $NaClO_4$ the ionic strength in experiment D was increased to $\mu = 0.104$, the concentration of $[Co(NH_3)_5NCS]^{+2}$ + Hg(II) being slightly reduced to 0.00194 f by the dilution. Data of experiment D are normalized to 0.002 f for comparison with experiment C. The data of experiments C and D indicate that increasing the ionic strength from 0.014 to 0.104 at constant acidity causes an increase in the cation–cation interaction (*i.e.*, increase in Y) and also an increase in the "effective" n from 1.4–1.5 to 2.0.

The effects noted above agree with predictions based upon the Debye–Hückel equation. At ionic strength of 0.1–0.2 and less, increasing μ should also increase the interaction between $[Co(NH_3)_5NCS]^{+2}$ and Hg(II), while at the same time repressing the hydrolysis of the latter.

$[Cr(NH_3)_5NCS](NO_3)_2$–$Hg(NO_3)_2$.—A study comparing this system with its cobalt counterpart is complicated by the instability of the thiocyanatopentaamminechromium ion, a weaker absorption band in the visible for measurement and more restricted limits of solubility (*vide supra*). Precipitation occurred in 0.002 f $[Cr(NH_3)_5NCS](NO_3)_2$ within a few minutes at concentrations of $HClO_4$ or HNO_3 exceeding 0.01 M, whereas 0.002 f $[Co(NH_3)_5NCS](NO_3)_2$ in 0.1 M $HClO_4$ was stable with respect to precipitation from 5 hr. to 1 day.

The continuous variation experiments, E and F of Fig. 5 were performed at measured pH's of 2.1 and 3.0, respectively, with the system 0.002 f in Cr + Hg. Since aquation of the interaction products is rapid in this system (see Fig. 3), it was necessary to follow the density change of each mixture for 30–40 min. and back-extrapolate the readings at each wave length to zero time of mixing. In experiment E, at a pH of 2.1, the maximum of the plot of Y *vs.* x for each of the wave lengths measured occurred at approximately 0.58 ($n = 1.4$). A ten-fold lowering of the acidity to a measured pH of 3.0 in experiment F caused a displacement of the maximum to approximately $x = 0.52$ ($n = 1.1$).

The similarity in type to the analogous cobalt system is apparent in the close agreement of the "effective" interaction ratios obtained in the solutions of the same measured acidity and ionic strength, *viz.*, experiments C (1.4–1.5) and E (1.4) and experiments B (1.0) and F (1.1).

$[Co(NH_3)_5NCS](NO_3)_2$–$AgNO_3$.—Figure 6 presents representative data from three continuous variations experiments (G, H and I) on the interaction of Ag(I) and $[Co(NH_3)_5NCS]^{+2}$ ions. Each mixture was shaken with nitrobenzene and centrifuged before measurement as already described on p. 2962. The interaction of Ag(I) ions with thiocyanato cations, unlike that of Hg(II) ions, is not complicated by hydrolytic phenomena since the pk value of the first hydrolysis constant for aqueous Ag(I) ion is greater than 11.[22] A single rather broad maximum in the curve of Y *vs.* x for each wave length measured occurs near or slightly above $x = 0.5$ in both experiments G and H. This is indicative of a rather highly dissociated 1:1 cation species with perhaps a small fraction of a 2:1 species also present. The effect of increasing the ionic strength is seen in the increase of Y, which is a measure of the magnitude of the cation–cation interaction.

In order to favor higher complexing as much as possible, the concentration of the system $[Co(NH_3)_5NCS]^{+2} + Ag^+$ was increased to 0.00371 f (experiment I of Fig. 6), the highest concentration feasible due to the limited solubility of the system. In this experiment the maximum of Y *vs.* x occurs at approximately $x = 0.58$ indicating an average interaction ratio of Co:Ag = 1.4:1.0.

Further evidence for the existence of a 2:1 species was obtained by observing the eleven solutions prepared for experiment I after 4 days. The relative amounts of buff-brown precipitate estimated for each of the mixtures were as follows (x:volume fraction of $[Co(NH_3)_5NCS]^{+2}$ in the mixture and amount of precipitate 0–10 in arbitrary units): 1.00, 0; 0.85, 5; 0.75, 7; 0.67, 10; 0.58, 3; 0.50, 3; 0.42, 2; 0.33, 1; 0.25, 1; 0.15, 1; and 0.00, 0. It is seen that precipitation was peaked at $x = 0.67$ where the ratio Co:Ag = 2:1.

$[Co(NH_3)_5NCS](NO_3)_2$–$AgNO_3$.—The interaction of this system (see Fig. 3) was found to be too weak for satisfactory study by the method of continuous variations.

***cis*-$[Co(en)_2(NCS)_2]NO_3$–$Hg(NO_3)_2$.**—Figure 7 illustrates three experiments, J, K and L, performed with this system. In each experiment the well-defined maximum indicates a 1:1 interaction species.

The insolubility of the 0.002 f system, *cis*-$[Co(en)_2(NCS)_2]NO_3$–$Hg(NO_3)_2$, in 0.1 M perchloric acid in the range between $x = 0.5$ and $x = 0.9$ (experiment L) probably is due to the existence of complexes containing Co:Hg ratios greater than one which are both much more dissociated and much less soluble than the 1:1 species.

At least one insoluble species may be a 2:1 complex. After performing experiment K (Fig. 7) the following experiment was performed with 0.005 f solutions of the parent *cis* complex and mercury(II) nitrate. Both solutions were also 0.5 M in $HClO_4$. Addition of the solution of *cis*-dithiocya-

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(21) Acidity measurements were made with a glass electrode and calomel cell having a NaCl bridge.

(22) J. Kasper, Thesis, Johns Hopkins Univ., 1941, p. 14.

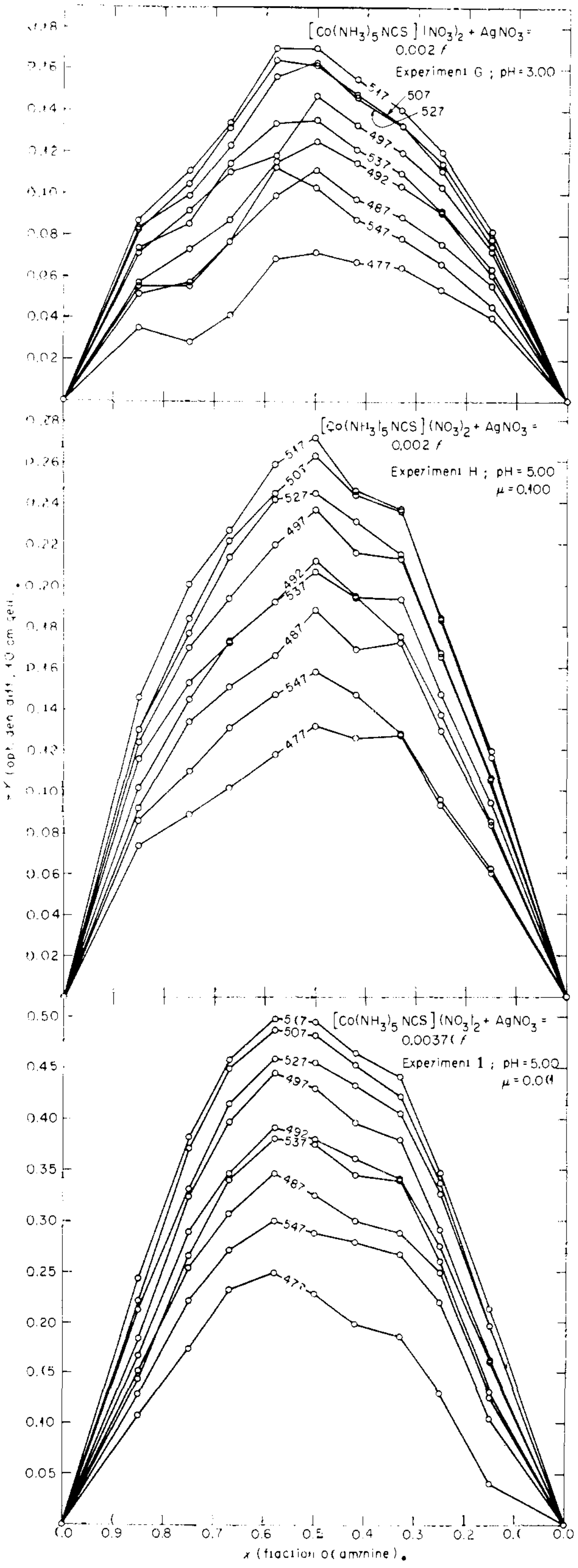

Fig. 6.—Continuous variations experiments with [Co(NH$_3$)$_5$-NCS]$^{+2}$ and Ag(I).

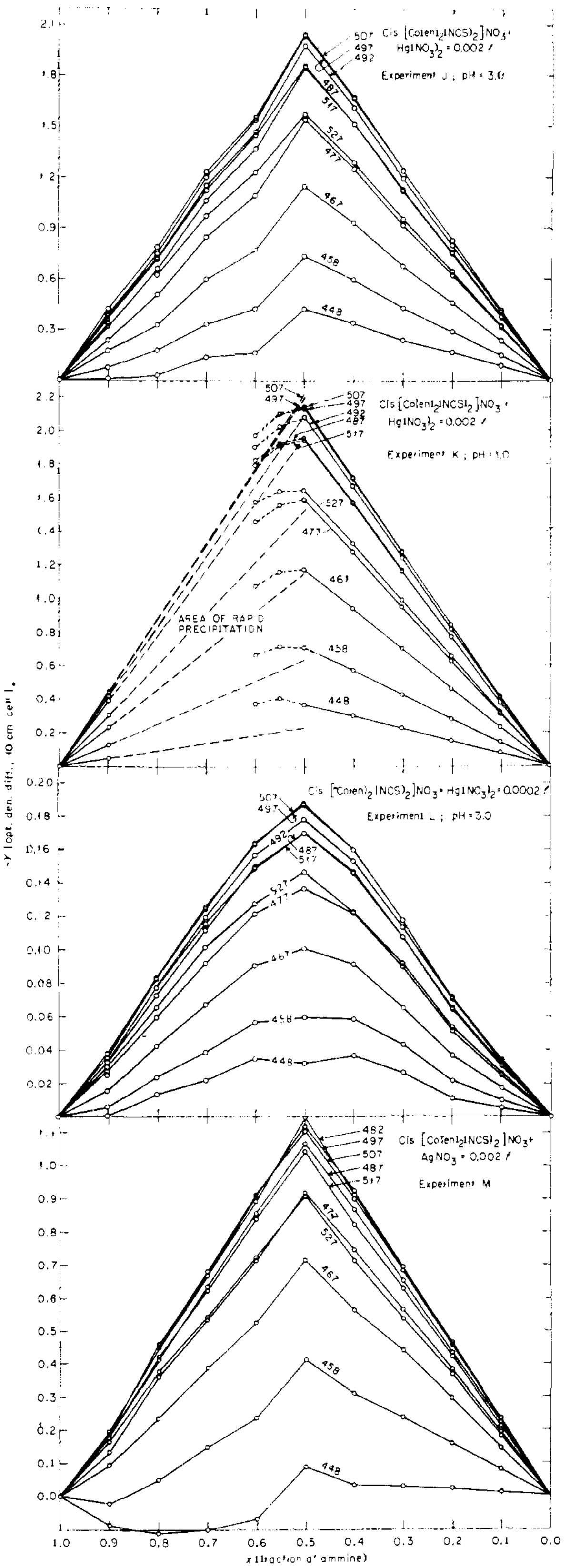

Fig. 7.—Continuous variations experiments with *cis*-[Co(en)$_2$(NCS)$_2$]NO$_3$ and Hg(II) or Ag(I).

nato complex ion to the equiformal solution of Hg(II) ion resulted in a clear yellow solution up to a 1:1 ratio of cations. The inception of precipitation was quite sharp as the 1:1 ratio was exceeded and continued until a cation ratio of 2:1 was reached, at which point precipitation was sharply complete and the supernatant solution was virtually colorless. Further addition of the orange solution of the parent complex produced no additional visible action. The precipitation was readily reversed by adding more Hg(II) ion, the orange-yellow precipitate completely redissolving as soon as the cation ratio again reached 1:1.

***cis*-$[\mathrm{Co(en)_2(NCS)_2}]\mathrm{NO_3}$–$\mathrm{AgNO_3}$.**—Figure 7 also gives the results of experiment M conducted with the 0.002 *f* system (Co + Ag) in water. The linearity of the *Y vs. x* plot and the position and sharpness of the maximum indicate existence of a single 1:1 addition species which is only slightly dissociated in 0.001 *f* solution.

***cis*-$[\mathrm{Cr(en)_2(NCS)_2}]\mathrm{NO_3}$–$\mathrm{Hg(NO_3)_2}$.**—A single experiment with the 0.01 *f* system (Cr + Hg) in 0.1 *M* $HClO_4$ was run. Immediate precipitation of a buff-colored complex occurred with all mixtures prepared in the range above $x = 0.5$. The data of solutions having $x = 0.5$ indicated a soluble, relatively stable 1:1 interaction species quite similar to the corresponding cobalt system.

Displacement of Cation Interaction Equilibria by Thiocyanate Ion

The equilibria between thiocyanato complex ions and either Ag(I) or Hg(II) ions were displaced by the addition of alkali thiocyanate to any of the yellow or orange-colored interaction solutions. Solutions containing Ag(I) and solutions containing Hg(II) in excess of 0.001–2 *M* gave a white precipitate of the respective thiocyanate which redissolved in a sufficient excess of thiocyanate ion, producing a clear solution the color of which appeared identical with that of the parent thiocyanato complex ion. Under 0.001 *M*, precipitation of $Hg(SCN)_2$ does not occur and the progress of de-coördination of the thiocyanatoammine may be followed conveniently with the spectrophotometer. It appears that quantitative displacement of this interaction system requires two moles of NCS per mole of Hg(II).

Discussion

The continuous variations experiments (Fig. 5–7) are interpreted in terms of equilibria involving, in general, thiocyanato–metal cationic species with interaction ratios of 1:1 and 2:1, respectively. These species absorb light at identical wave lengths in the visible and their spectra are in effect a perturbation of the spectrum of the parent thiocyanato cation.

The experiments definitely show that the addition reactions are reversible, in contradiction of the original claim of Werner. The rounded peaks of the *Y vs. x* curves in the continuous variations experiments may be best interpreted as evidence of considerable dissociation at the stoichiometric ratios. The density differences are too small, however, to permit reliable calculation of equilibrium constants.

The structure of a non-labile thiocyanato–metal complex has not been analyzed in detail by diffraction methods. Octahedral coördination of the ligands in complexes of tervalent chromium and cobalt is established but as yet there are no specific X-ray data concerning the orientation of a coördinated NCS group, and its colinearity or non-colinearity with the central atom of a thiocyanatoammine. The formation of bonds, by either nitrogen or sulfur, at large angle to the N–S direction, such as observed, for example, in isothiocyanic acid[23] (130° for H–N–C), or the tetrahedrally coördinated $Hg(SCN)_4^{-2}$ [24] (102° for Hg–S–C) does not seem to be tenable from steric consideration of the position of ammonia or ethylenediamine ligands. It seems probable that the NCS group is essentially colinear with the central atom in the thiocyanatoammine and that structures involving ionic bonds between NCS and metal contribute largely to the normal state of these ions.

With regard to orientation, the existence of the isothiocyanato structure in all the thiocyanatoammines of Cr(III) and Co(III) may be inferred from the evidence available. Hydrolytic oxidation of thiocyanatocobalt(III) complexes to the corresponding ammines in the presence of acid *vide supra* is strong evidence favoring the Co–N bond. The silvermonothiocyanatocobalt(III) type of interaction has been expanded by the present study so that it now includes not only Hg(II) ions plus the isomeric dithiocyanatoamminecobalt(III) ions but also the similar series of thiocyanato cations of tervalent chromium. The nature of these reactions, and the identity of type established between the cobalt and chromium series may be used to infer that the structure of the latter also involves a Cr–N link.

Another argument favoring the iso-orientation is found in the color of the thiocyanato complexes. Replacement of one ammonia of hexaamminecobalt(III) or chromium(III) by NCS causes less shift toward the red in the visible absorption than would be expected for a VI-b element. The thiocyanatopentaammines are yellow-orange in color, whereas nitrito-, hydroxo-, carbonato- or sulfitopentaammines are pink to deep red cations. The latter named ions are coördinated to the central atom through oxygen or sulfur. The unstable red nitritopentaamminecobalt(III) ion changes slowly (at room temperature) to yellow-brown nitropentaamminecobalt(III) in which the nitrogen coördinates the central atom.

Steric considerations as well as the comparative electronegativities of N and S favor the iso-orientation because of the smaller size and greater electronegativity of the nitrogen.

Finally, the metal–thiocyanato complex interaction itself favors the isothiocyanato structure for the parent complexes. Both cobalt(III) and chromium(III) have a manifest tendency for coördination of nitrogen, while silver(I) and mercury(II) on the other hand in their compounds have an inclination for coördination of sulfur. The preference of Hg(II) and Co(II) for coördination of the S and N ends, respectively, of the NCS radical is well demonstrated by the results of

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(23) G. C. Dousmanis, T. M. Sanders, C. H. Townes and H. J. Zeiger, *J. Chem. Phys.*, **21**, 1416 (1953).

(24) H. Scouloudi, *Acta Cryst.*, **6**, 651 (1953).

recent single crystal studies of $Co[Hg(SCN)_4]$,[25] $[Cu(en)_2][Hg(SCN)_4]$[24] and $K_2[Co(NCS)_4 \cdot 4H_2O$.[26] The orientation of the linear NCS radicals in each of the lattices is such that the nearest neighbors of Hg are S atoms while the nearest neighbors of Co in each case are N atoms.

If the parent cations are assumed to have the isothiocyanato structure, it appears from this study that a Hg(II) ion (and to a less degree a Ag(I) ion) may interact with the highly polarizable sulfur of either one or two thiocyanato groups. One may speculate that the bonds formed make use of the co-linear s or sp hybrid orbitals of dicovalent Hg(II) plus sp orbitals of the sulfur, the latter directed at large angle to C–S (*viz.*, 100–130°).

The picture of the 1:1 and 2:1 interaction species involving the monothiocyanatopentaammines is straightforward. Further, the especially stable 1:1 soluble species involving *cis*-dithiocyanato cations suggest the presence of rings involving one or two Hg(II) or Ag(I) ions, respectively, bonding the sulfurs of one or two dithiocyanato cations, while the slightly soluble, less stable 2:1 species possibly consists of a dichelate cation having the four sulfurs tetrahedrally bonded to a single Hg(II) ion. The very much smaller solubilities of the *trans*-dithiocyanatobis-(ethylenediamine) interaction species may be attributed to a tendency of the *trans* structures to form insoluble polymeric chains involving alternate links of complex and metal cations.

The isolation and characterization of solids was not a prime objective in these studies since we were concerned with the nature of the thiocyanato complex–metal interaction cations associated with the color changes observed in solution. Preliminary experiments with the monothiocyanatopentaammines and Ag(I) and Hg(II) indicated that the empirical composition, crystal form and homogeneity of the products isolated were sensitive to conditions such as temperature and concentration of constituents. It appears possible from the observed weak nature of these interactions that the ions which exist in solution bear no direct relation to (and therefore cannot be inferred from) the crystalline isolates. However, such might well constitute a separate study in itself.

In conclusion, the interaction of a thiocyanato complex cation with either Ag(I) or Hg(II) cations is rather unique in type. Perhaps the closest analogy is found in the addition of hydrogen ion to a hydroxo or carbonato cation (*e.g.*, $[Co(NH_3)_5OH]^{+2}$ or $[Co(NH_3)_5CO_3]^{+1}$) to form the corresponding aquo or hydrocarbonato cation. The blue shift which is observed in the absorption of the parent complex upon adding acid is immediate and quite similar to the shift observed, for example, in a solution containing $[Co(NH_3)_5NCS]^{+2}$ in the presence of Ag(I) or Hg(II) cations. Further analogy is seen in the effect of the central atom. Just as $[Co(NH_3)_5OH]^{+2}$ has a greater affinity than $[Cr(NH_3)_5OH]^{+2}$ for hydrogen ion[27] similarly $[Co(NH_3)_5NCS]^{+2}$ interacts more strongly than $[Cr(NH_3)_5NCS]^{+2}$ with either silver or mercuric ions.

Acknowledgment.—One of us (W.C.W.) gratefully acknowledges the encouragement and interest of Dr. R. W. Stoughton, Oak Ridge National Laboratory, during the latter phase of this work.

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

Mixed Ligand Complexes of Nickel(II) with Cyanide and 1,10-Phenanthroline

BY ALFRED A. SCHILT

RECEIVED DECEMBER 17, 1958

Attempts to prepare the conceivable mononuclear mixed ligand complexes of nickel(II) with cyanide and 1,10-phenanthroline (ophen) did not yield any of the anticipated products but resulted instead in the isolation of three different complex compounds. The empirical formulas of these insoluble substances are Ni_2 $ophen_3(CN)_4(H_2O)_4$, Ni $ophen(CN)_2(H_2O)$ (a yellow solid) and Ni $ophen(CN)_2(H_2O)_{0.5}$ (a lavender solid). Chemical, spectrophotometric and magnetic data indicate the identity of the first to be $[Ni\ ophen_3][Ni(CN)_4] \cdot 4H_2O$; the latter two are mixed ligand complexes which, in view of their peculiar properties, may involve cyanide bridging groups.

Introduction

Coördination of bivalent nickel by 1,10-phenanthroline gives rise to a paramagnetic octahedral complex; whereas in the case of cyanide coördination a diamagnetic square coplanar complex of nickel(II) results.[1] It is therefore of interest to learn whether or not one or more complexes of nickel(II) can be obtained which involve both of these very dissimiliar coördinating groups. If any mixed ligand complexes of nickel(II) with cyanide and 1,10-phenanthroline do exist, it is anticipated that their properties may prove to be of unusual interest in regard to possible applications and theoretical significance.

Previous studies have revealed the existence, identities and properties of the mixed ligand complexes of iron(II) with cyanide and 1,10-phenanthroline.[2–4] The peculiarities observed for this series of mixed ligand complexes together with

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