condensation product from 2-propionyl-6-methoxynaphthalene (V) and dimethyl succinate, reduces the total number of steps of the synthesis to *seven* starting with β-methoxynaphthalene.

A similar cyclization study has been made also with the lower homolog VI (CH_3 in place of C_2H_5) which was obtained in two diastereoisomeric forms. The stereochemical integrity was retained throughout both the cyclization step to give two forms of the keto ester, and the reduction step affording two stereoisomeric forms of VII (CH_3 in place of C_2H_5). The structure of these products was shown by dehydrogenation experiments.

The cyclization method was also extended to the tetrahydro half-ester IX which gave the expected product of linear cyclization, namely, X.

PHILADELPHIA, PA.
MADISON, WISCONSIN RECEIVED JULY 31, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Spectrophotometric Studies of Cobalt(II) Thiocyanate Complexes in Organic Solvents

BY LEONARD I. KATZIN AND ELIZABETH GEBERT

Cobaltous nitrate dissolved in organic solvents gives a red to magenta solution, due to formation of undissociated cobaltous nitrate.[1] Addition of lithium nitrate or tetrabutylammonium nitrate to the solution in acetone, or tetrabutylammonium nitrate to the solution in *t*-butyl alcohol, gives a trinitrate complex which in the alcohol, at least, is relatively weak.[1] Cobalt chloride dissolved in most organic solvents gives an intense blue color, apparently associated with formation of entities corresponding to CoX_2Cl_2, where X represents a solvent molecule.[2] With a weak electron donor such as acetone or tetrahydrofuran as the solvent, addition of lithium chloride gives a series of forms, $CoXCl_3^-$ and $CoCl_4^=$ with characteristic absorptions. In alcohol solutions, $CoCl_4^=$ is apparently unobtainable, and the $CoXCl_3^-$ achieved only with difficulty. Both anion and solvent effects are therefore identifiable.

The thiocyanate complex of cobalt(II) is rather stable, from the criterion of formation of salts with $Co(SCN)_4^=$ groupings, etc., in comparison with the other complexes mentioned. These salts are blue, as are solutions of cobalt with thiocyanate in organic solvents. The comparison of spectra and complexes with those of the nitrate and chloride salts is therefore of interest.

Procedures

Spectrophotometric measurements were made with the Beckman model DU quartz spectrophotometer. The density scale of the instrument was calibrated with standards obtained from the National Bureau of Standards. Density settings were found reproducible to 0.002 density unit.

Cobalt perchlorate was prepared from the carbonate and perchloric acid, and recrystallized twice. The solid so obtained was the hexahydrate. Lithium thiocyanate was prepared in acetone solution by metathesis of potassium thiocyanate and lithium nitrate in acetone solution. The precipitated potassium nitrate was removed by centrifugation, and the thiocyanate concentration checked by titration against a silver nitrate standard. The preparation of the lithium salt was advisable, to avoid precipitation of potassium perchlorate on mixing with the cobalt solutions. The thiocyanate solution is colorless.

Solvents used were the commercial pure products. Stock solutions were made of the salts in the desired solvents, and aliquot dilutions made for spectrophotometric study. Cobalt concentrations were determined for the stocks by standard electrodeposition procedures. Pyridine solutions were made from weighed portions of the liquid. Thiocyanate solution preparation and standardization has been described above.

Experimental

Job[3] has described a procedure for determining the formula of an additive complex which he has called the method of continuous variations, and which we have extended to the case of formation of more than one complex.[1,4] In brief, when stocks of the two reagents, of equal concentration, are mixed in various proportions, the concentration of the complex is at a maximum when the reagents are in the ratio of their stoichiometric proportions in the complex. When more than one complex is formed,[1] the lowest complex is at a maximum at a reactant ratio less than the stoichiometric, the highest complex is a maximum at a ratio greater than the stoichiometric, and the direction and extent of deviation of any intermediate complex from the stoichiometric maximum depends in detail on the system. When changes in the absorption of the mixtures are used to measure the concentrations of the complexes, the maxima in the absorption changes will in general not fall at the maxima in the complex concentrations, except when a wave length is chosen at which the absorption is ascribable almost solely to a single complex. Otherwise there may be one, two or three maxima and/or minima in the deviation plot; for details one is referred to the original.[1]

On applying this technique to mixtures of cobalt perchlorate and lithium thiocyanate in acetone, one finds, on plotting the excess optical density over that of the components against the thiocyanate formal concentration (Fig. 1), that one is dealing with both a trithiocyanate and a tetrathiocyanate complex. The wave lengths chosen for Fig. 1 were based on a plot (Fig. 2) of logarithm of

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[1] L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5455 (1950).

[2] L. I. Katzin and E. Gebert, *ibid.*, **72**, 5466 (1950).

[3] P. Job, *Ann. chim.*, [10] **9**, 113-134 (1928).

[4] W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 437 (1941).

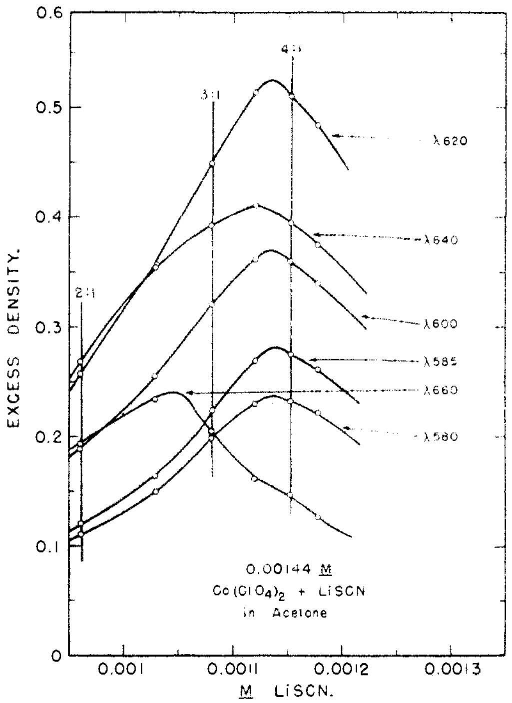

Fig. 1.

formal extinction coefficient against wave length, the semi-logarithmic plot being used to enable shape comparisons of the curves to be made. As can be seen, the shapes of the curves from ratios of 1 thiocyanate to 2.5 thiocyanates per cobalt are essentially identical. The curve shown for the ratio 6:1 is indistinguishable from those for 4.5:1 and 12:1. Considering Figs. 1 and 2 together, therefore, one concludes that both the trithiocyanate and the tetrathiocyanate are relatively stable complexes in acetone, and that if a dithiocyanate forms, its absorption and concentration can be significant and recognizable only at low SCN:Co ratios, *i. e.*, 1:1 or less. The maximum extinction coefficient obtained at 620 mμ is about 2150 (0.2 millimolar cobalt).

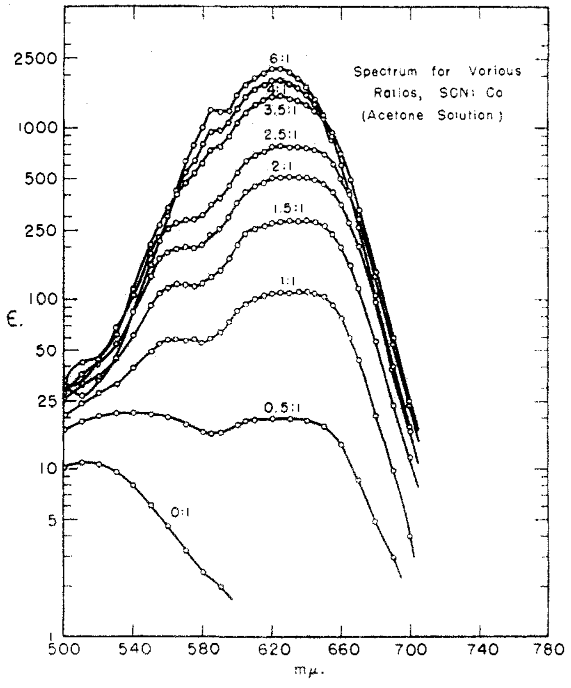

Fig. 2.

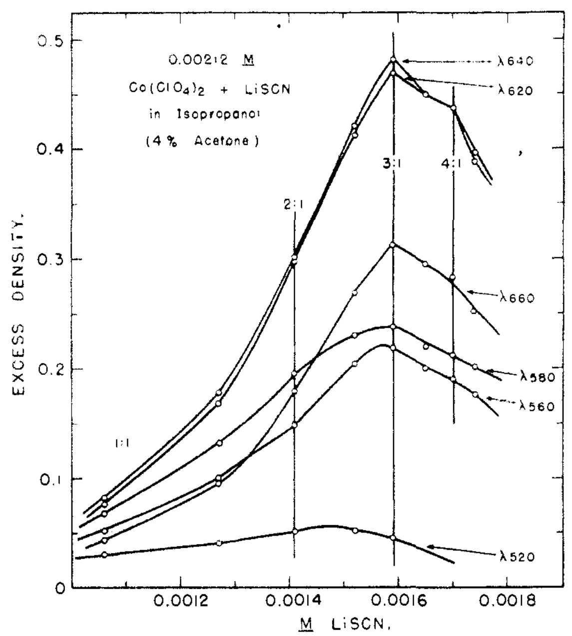

Fig. 3.

In isopropyl alcohol (containing 4% of acetone by volume, due to the thiocyanate stock being made up in acetone) one fails to obtain the spectrum recognized in the acetone solution as due to the tetrathiocyanate (Fig. 3). There is a small but perceptible change in shape between the extinction curves for the ratio 1:1 and 4:1 thiocyanates per cobalt. The method of continuous variations shows (Fig. 4) that the principal absorption is due to the tri-

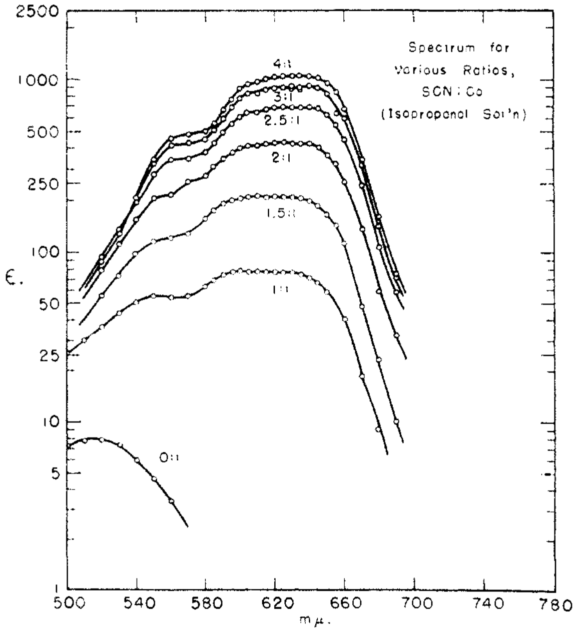

Fig. 4.

thiocyanate complex, but there is a noticeable contribution of a dithiocyanate form detectable at 520–560 mμ. The differences in the two curves seem to be mainly a shift to longer wave lengths of 10–20 mμ for the higher complex curve, and an alteration in the intensity ratio of the longer wave length plateau to the shorter, from about 1.4 for the dithiocyanate to 2.1 for the trithiocyanate. Higher ratios than 4:1 for the thiocyanate to cobalt ratio fail to produce intensity or spectrum change, and the maximum extinction coefficient found is about 1060.

t-Butyl alcohol (with 4% by volume of acetone) shows spectra very much the same as those shown in the isopropyl alcohol solution (Fig. 5), and the contribution of both dithiocyanate and trithiocyanate complexes can be demonstrated (Fig. 6). An essential difference between the two alcohols is the lower dielectric constant of *t*-butyl alcohol (10 as against 18). Because of this, the dithiocyanate complex appears more stable in the *t*-butyl alcohol solution, with a correspondingly higher extinction for thiocyanate to cobalt ratios up to 2:1. This influence shows also as a more marked contribution of the dithiocyanate complex in the continuous variations experiment (Fig. 6). The ultimate extinction coefficient obtained for the trithiocyanate complex is the same in the two alcohols.

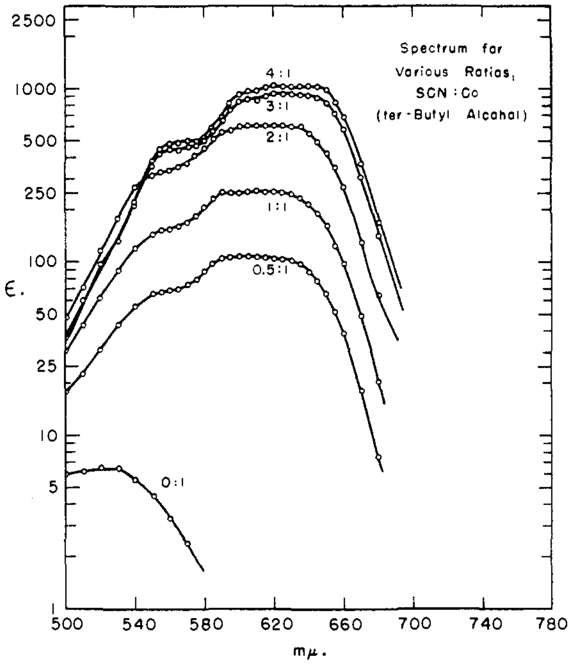

Fig. 5.

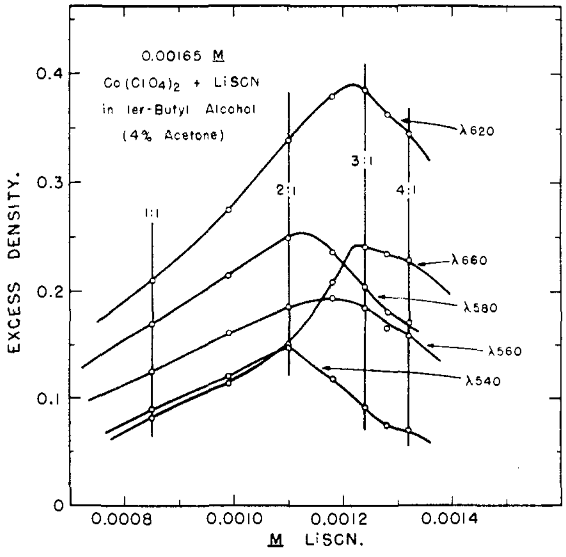

Fig. 6.

A comparison of the absorption curves in the several solvents is of interest. Aside from the final tetrathiocyanate curve, found only in acetone, there are small but detectable differences in the absorptions of the trithiocyanate complexes in acetone and in the alcohols. These consist of a difference in the intensity ratio of the long-wave length and shorter-wave length peaks, and in the sculpturing of the smaller peak, with maximum at about 565 mμ. These differences are of the same type as found in the case of the chloride complexes,[2] which have been related to differences in the structural group of the solvent molecule bound to the metal atom. There is a question in the case of the thiocyanate as to the extent that the first of these differences, that in the relative peak heights, is influenced by formation of small fractions of the very highly absorbing tetrathiocyanate complex. Another difference between acetone and the alcohols, of course, is the ready formation of the tetrathiocyanate in acetone, and its essential non-formation in the alcohols. A similar phenomenon in the case of the chlorides was shown to be due to the difference in base strengths of ketone and alcohol groups.[2]

After the completion of this work, there appeared a paper on the cobalt thiocyanate complexes in acetone by Babko and Drako.[5] Working with a photometer and band-pass filters, they report two complexes, the $Co(CNS)_4^{=}$ and a $CoCNS^+$. Their failure to find the trithiocyanate complex is obviously due to their procedure, with measurements made only at band-pass maxima as-

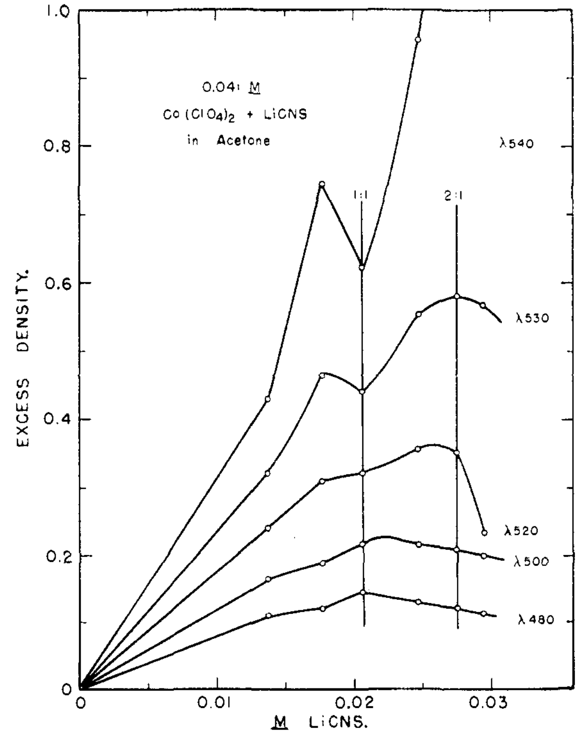

Fig. 7.

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[5] A. K. Babko and O. F. Drako, *J. Gen. Chem.* (*U. S. S. R.*), **19**, 1809 (1949).

sumed to be 500, 530, 570 and 650 mμ, respectively. Another possibility was considered with reference to their $CoCNS^+$ complex: the solutions used in their experiments were 0.05 *M*, while ours have been not more than 0.002 *M*. It therefore seemed possible that a relatively unstable $CoCNS^+$ complex would not have appeared in our experiments with dilute solutions, but might be revealed at the high concentrations. Experiments carried out by the method of continuous variations at a concentration of 0.04 *M* have shown this to be the case (Fig. 7), evidence for the $CoCNS^+$ complex being found at wave lengths below 550 mμ. With absorption in this region, the complex of course does not contribute to the blue color shown by the other thiocyanate complexes. This would be in agreement with the expectation that such a complex should be hexacoördinate and of the "red" type, rather than tetracoördinate "blue" type[2] as is the tetrathiocyanate complex. It should be pointed out that the complex probably should be written $Co(CNS)(ClO_4)\cdot 4$ solvent, since cobalt perchlorate is only partially dissociated in acetone.[1]

It seems hardly necessary to emphasize here, what is true for the several cobalt salts investigated, and probably also is true for many complexes of other metals: when an analytical method depends on maximum complex formation, ketone medium (as contrasted with aqueous or alcoholic) may be expected to give greatest sensitivity. This is especially true for colorimetric procedures in which the extinction coefficients of the highest complex are greater than those of other complexes which may be formed.

Summary

1. In very dilute solution in acetone, cobalt(II) yields trithiocyanate and tetrathiocyanate complexes.

2. In dilute solution in isopropyl or *t*-butyl alcohol, only dithiocyanate and trithiocyanate complexes are found.

3. The extinction coefficient of the tetrathiocyanate complex is about twice that of the trithiocyanate complex.

4. In relatively concentrated solution in acetone, an unstable complex involving a single thiocyanate group can be identified.

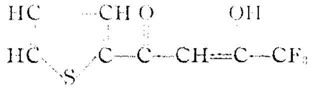
CHICAGO 80, ILLINOIS RECEIVED MAY 29, 1950

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

Chemistry of Thorium in Aqueous Solutions. I. Some Organic and Inorganic Complexes[1]

BY R. A. DAY, JR.,[2] AND R. W. STOUGHTON

Fry, Barney and Stoughton[3] have recently reported a number of equilibrium constants for the formation of thorium–iodate complex ions. These constants were determined from solubility measurements and solvent extraction data. The solvent extraction method used involved the determination of the distribution ratios between aqueous solutions containing thorium and iodate and benzene solutions containing thenoyl trifluoroacetone (TTA) as a chelating agent. The latter compound has the following structure in the enol form



This method has also been used to determine the equilibrium constants of some zirconium complexes.[4]

The present work was undertaken to determine the stability of complex ions formed between thorium and the anions of several monobasic acids. The acids studied were hydrochloric, nitric, chloric, bromic, hydrofluoric, chloroacetic, dichloroacetic, trichloroacetic, acetic and formic. The TTA extraction method was used throughout. The equation for extraction can be written as

$$Th^{+4} + 4HT_b \rightleftharpoons ThT_{4b} + 4H^+ \quad K_T \qquad (1)$$

where HT stands for TTA, T for the enolate ion of TTA, K_T for the equilibrium constant of the reaction, and the subscript *b* indicates that the species involved is in the benzene phase. It is assumed that ThT_4 is the only thorium-containing species in the organic phase and that it exists predominantly in that phase.[5] The work of King and Reas[6] and of Zebroski and Alter[7] shows that 2% of the TTA present is in the aqueous phase under our conditions and that this figure is constant TTA concentration and constant ionic strength in the aqueous phase.

To illustrate the calculations, let us consider the case of thorium complexed by the anion of the weak acid, HX. Considering only two complex ions to be formed, one can write the equations

$$Th^{+4} + HX \rightleftharpoons ThX^{+3} + H^+ \quad k_1 \qquad (2)$$

$$Th^{+4} + 2HX \rightleftharpoons ThX_2^{+2} + 2H^+ \quad k_2 \qquad (3)$$

where k_1 and k_2 are equilibrium constants for the reactions. The ratio of thorium in the aqueous

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(1) The work covered in this paper was carried out under the auspices of the Atomic Energy Commission at Oak Ridge National Laboratory.

(2) Chemistry Department, Emory University, Emory University, Ga.

(3) Fry, Barney and Stoughton, "Atomic Energy Commission Report," AECD-2429 (1948).

(4) Connick and McVey, THIS JOURNAL, **71**, 3182 (1949).

(5) Work of Connick and co-workers indicate this assumption to be valid for other tetravalent cations. Also W. C. Waggener and R. W. Stoughton (private communication) have found that the dependence of thorium extraction on both TTA and hydrogen ion is fourth power in the range of 0.1 to 0.5 *M* $HClO_4$ and an ionic strength of 0.5. Thus since all thorium is in the +4 state, the extracted species must be ThT_4.

(6) King and Reas, "Atomic Energy Commission Report," BC-69, July, 1947.

(7) Zebroski and Alter, private communication