DITHIOOXAMIDE AS AN ANALYTICAL REAGENT

by

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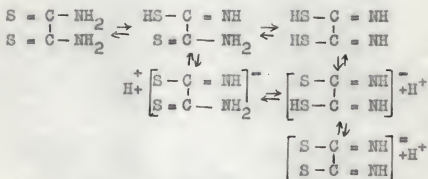KANSAS STATE COLLEGE
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Dithiooxamide, which is commonly called rubeanic acid, is a weakly acidic compound, capable of chelate formation with a number of metallic ions. Presumably, the acidic character of rubeanic acid is attributable to the tautomerism existing between the diamido (base), amidoimido (semi-acid), and diimido (acid) forms (12).

$$\begin{array}{ccc}
S = C-NH_2 & HS-C = NH & HS-C = NH \\
S = C-NH_2 & S = C-NH_2 & HS-C = NH
\end{array}$$

$$H^+ \begin{bmatrix} S-C = NH \\ S = C-NH_2 \end{bmatrix}^- \rightleftharpoons \begin{bmatrix} S-C = NH \\ HS-C = NH \end{bmatrix}^- +H^+$$

$$\begin{bmatrix} S-C = NH \\ S-C = NH \end{bmatrix}^= +H^+$$

It follows from these equilibria that to increase the concentration of the rubeanate ion, removal of hydrogen ion is required, and that as an analytical reagent rubeanic acid is most sensitive in basic solutions. However, rubeanic is unstable in alkaline media, so that most determinations with this reagent are made in neutral or slightly acid solutions.

Rubeanic acid reacts only with colored, transition metal ions to form intensely colored rubeanates. For the divalent ions of copper, cobalt, nickel, and palladium, the quantitatively precipitated rubeanates are presumed to have an inner complex type of structure, in which Me represents the divalent metal. In this formula, originally proposed by Ray (29), two over-

lapping five-membered rings are formed, which would be a very

$$H-\overset{5}{N}=\overset{4}{C}-\overset{3}{C}=NH$$
$$\underset{\substack{S \quad S2 \\ \diagdown \diagup \\ Me \\ 1}}{| \quad |}$$
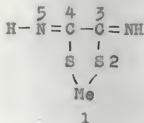
stable configuration. It is known that the solid metal rubeanates
are quite resistant to mineral acids in concentrations as great
as 1:1. Aside from a few determinations of empirical formulae
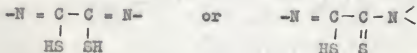for metal rubeanates, there is little direct experimental support
for a particular structural formula for these compounds. From
magnetic susceptibility measurements on nickel rubeanate, Voznes-
enskii (43) concluded that a simple structure like that above is
not adequate, but a high molecular weight polymeric form is re-
quired. For the reaction of platinum and palladium with rubeanic
acid, Wolbling and Steiger (45) suggested the metal reacts with
the semi-acid form of dithiooxamide, giving the compound:

$$\begin{array}{l} S = C-NH_2 \\ \quad | \quad\quad\quad \vdots\; Pd/2 + 1 \text{ Rubeanic acid;} \\ HN = C-S \end{array}$$
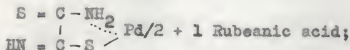
However, the structure with palladium coordinated with two
moles of rubeanic acid cannot be ruled out. The N, N -dialkyl
and diphenyl derivatives of dithiooxamide react in the same
manner as the parent compound, (12, 46) thus establishing con-
clusively that the metal reacts with the

$$-N = \underset{\substack{| \\ HS}}{C}-\underset{\substack{| \\ SH}}{C} = N- \qquad \text{or} \qquad -N = \underset{\substack{| \\ HS}}{C}-\underset{\substack{|| \\ S}}{C}-N\!<$$

groups. However, experimental evidence has failed to distin-
guish between these possible structures for the rubeanates.
Bridge structures involving four and five-membered rings have
been proposed (11, 18).

Only a very limited amount of quantitative information con-
cerning the ionization of rubeanic acid and the solubility and
stability constants for metal rubeanates is available. From
solubility behavior, Voznesenskii (43) estimated the dissocia-
tion constant of dithiooxamide to be 3.0×10^{-10}. Yaffe and
Voigt (47) determined K_a, K_{sp}, and the molar solubility of rube-
anic acid, using a potentiometric titration method. A thorough
spectrophotometric investigation of the reaction between ruthe-
nium (III) and rubeanic acid was made by Yaffe and Voigt (47).
In this case the metal rubeanate does not precipitate, but forms
an intense blue color in solution. Ruthenium to dithiooxamide
ratios of 1:1 and 1:3 were found, but no evidence for a 1:2 com-
plex was reported. The dependence of the equilibrium upon hy-
drogen ion concentration was demonstrated, and the formation
constants given for the two complexes are $K_1 = 2.4 \times 10^{13}$ and
$K_3 = 5.8 \times 10^{24}$.

Although previous investigators have demonstrated that di-
thiooxamide is a highly sensitive and selective analytical rea-
gent, its applications have been based upon empirical conditions
with neither an adequate representation of the reactive species
of the reagent nor a conclusive picture of the products formed.
Therefore, the purposes of the study reported herein are: (1)
to establish the identity of the reactive species of dithiooxamide

existing in solution (with supporting quantitative data where
possible); (2) to arrive at reasonable structures for the metal
rubeanates, with particular attention to those of copper, cobalt,
and nickel; (3) to evaluate solubility product constants for
these metal rubeanates; and (4) to assemble a comprehensive
bibliography on the analytical applications of dithiooxamide.

ANALYTICAL APPLICATIONS OF RUBEANIC ACID

It is reported by Ray (29) that the potential analytical
application of dithiooxamide was first noted in 1825 by Wohler,
who observed that this compound precipitated copper, silver,
mercury, and lead from solutions of their salts. However, it
was almost one hundred years before any further study of the
reaction of dithiooxamide with metallic ions was made. Ray and
Ray (29) and Jensen (18) demonstrated that copper, cobalt, and
nickel are precipitated quantitatively with rubeanic acid, and,
from elemental analysis of the precipitates, they assigned a
general structural formula to the metal rubeanates. Low con-
centrations of the rubeanates can be kept in solution by employ-
ing mixed solvents with pyridine, dioxane, or acetone (46).

Precipitate formation between rubeanic acid and a number of
other metallic ions has been reported. Ayres and Tuffly (3)
used this reagent for the precipitation of palladium at pH 3.0,
in the presence of cobalt, nickel, and platinum metals, with
the exception of platinum itself. Under the conditions of this
method, rubeanic acid forms precipitates with platinum, gold,
iron, (II), copper, and chromium (III). Stable rubeanates are

precipitated with mercury (I), cadmium, and zinc according to Ray (28), while Voznesenskii (43) reported unstable products with iron (III) silver, mercury (II), and lead. The unstable rubeanates appear to hydrolyze rapidly to the corresponding metal sulfide and oxamide. For palladium and gold, the composition of the precipitated rubeanates is markedly dependent upon the pH of the medium (7).

Most of these precipitation reactions with rubeanic acid have little analytical importance. Rubeanic acid offers no significant advantage for the precipitation of the divalent metals with which it reacts, and the gummy, difficultly filterable precipitates are rather undesirable for gravimetric or isolation procedures. With the exception of palladium, few attempts have been made to improve the conditions for precipitation of metal rubeanates. Group precipitation of copper, nickel, cobalt, zinc, and cadmium have been used to separate these metals prior to their polarographic determination (33).

The major analytical utility of rubeanic acid is found in the detection of trace amounts of the metallic ions with which it reacts to form intensely colored precipitates or solutions. Diphenyldithiooxamide has been used for spot test detection of several metals in basic media (46). Other spot test procedures developed by Feigl (12) which use dithiooxamide are : (1) the detection of ruthenium, platinum, and palladium (42) in strongly acid solutions, without interference by osmium and other platinum group metals; (2) the detection of cobalt, with copper and nickel interferences; and (3) the detection of nickel in the presence of

moderate amounts of copper and cobalt. In general, rubeanic acid is more sensitive for detecting these metals than any other spot test reagent employed. A mixture of rubeanic acid and trisodium pentacyanominoferrate was used as a spot test reagent for twenty elements and the rare-earths (15). Rubeanic acid has been used as a spray reagent for copper, cobalt, and nickel·in paper chromatographic resolution of mixtures of these elements (41), and paper impregnated with cuprous rubeanate can detect the presence of oxidants (7).

Potentiometric (23) and amperometric (49) determinations of copper titrated with dithiooxamide are highly accurate, and can be performed without effect from ions that normally interfere in colorimetric measurements of the same reaction.

Several colorimetric procedures using rubeanic acid have been devised. Willard, Mosher, and Boyle (44) determined copper in magnesium and magnesium alloys, using a buffered system. To prevent the precipitation of copper rubeanate, gum arabic was added to stabilize the colloidal dispersions. Malonic acid prevented the interference of aluminum, bismuth, and ferric iron. A similar method has been used to determine copper in steels (20), the major alteration being the elimination of iron interference by oxidation to the ferric state and complexation with citrate, phosphate, or tartrate (6). This method for copper has also been used to determine the element in industrial wastes (17) and in medicinal iron preparations (1), and adapted to determining copper in aluminum alloys (21, 37). The blue complex formed by ruthenium (III) and dithiooxamide has been applied to the spec-

trophotometric determination of ruthenium in the presence of other platinum group metals (4). The stable complex is remarkably free of interference by other elements of this group, osmium being the only exception. Osmium is removed by distillation as the tetraoxide. Palladium rubeanate can be extracted into isoamyl alcohol without interferences if vereene is present (46).

RUBEANIC ACID AS AN ACID IN AQUEOUS AND NONAQUEOUS MEDIA

Reliable values for the acid dissociation constants are necessary for the calculation of solubility product and stability constants for metal rubeanates. In aqueous solutions rubeanic acid is a weak, slightly soluble acid, the acid strenth being too small to permit its titration with strong bases. A simple, relatively reliable method for the simultaneous estimation of the ionization constant, solubility product, and solubility for slightly soluble weak acids from a single potentiometric titration has been developed by Back and Steenberg (5). The essential features of this method are given below.

Method of Back and Steenberg

A known quantity of weak acid is dissolved in a known excess of standard base. This solution is then titrated potentiometrically with a standard acid. At the beginning of the titration, the weak acid is in the form of its soluble salt in a slight excess of base. After this excess base is neutralized, a known amount of titrating acid, having concentration C is

added and the pH measured. This process is repeated until floc-
culation occurs. From each of these measurements, a value for
pKa can be calculated. Essentially, it is the problem of hydrol-
ysis of the salt of a weak acid and a strong base. The concen-
tration of the salt is equivalent to the known concentration of
weak acid added originally, Ca, and C_H is the hydrogen ion con-
centration and C_{OH} the hydroxyl ion concentration.

$$(1) \quad HA \rightleftarrows H^+ + A^-$$
$$(2) \quad A^- + H_2O \rightleftarrows HA + OH^-$$
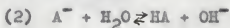
After the titration has proceeded beyond the point at which
precipitation begins, the solubility product K_{sp} can be evaluated.

$$pK_{sp} = pH - \log (C_a + C_H - C - C_{OH}) + \frac{0.5 \sqrt{u}}{1 + \sqrt{u}}$$

The molar solubility S then is easily calculated by

$$S = \frac{K_{sp}}{K_a}$$

This method developed by Back and Steenberg has been applied
to dithiooxamide by Yaffe and Voigt (47). It was stated that
dithiooxamide behaves as a monobasic acid, although no experi-
mental evidence was given to support this contention. Values
for the constants K_a, K_{sp}, and S_{HA} were determined at ionic
strength 0.01, and 1.0, the latter being maintained with sodim
perchlorate.

Table 1. Results of Yaffe and Vogt.

Quantity:	$\mu = 0.01$	:	$\mu = 1.0$
K_a	$1.28\ (\pm 0.04)\ \times\ 10^{-11}$		$3.78\ (\pm 0.04)\ \times\ 10^{-11}$
K_{sp}	$3.94\ (\pm 0.12)\ \times\ 10^{-14}$		$6.27\ (\pm 0.14)\ \times\ 10^{-14}$
S_a	$3.07\ (\pm 0.04)\ \times\ 10^{-3}$moles/l.		$1.66\ (\pm 0.03)\ \times\ 10^{-3}$moles/l.

Evaluation of K_a, K_{sp}, and Molar Solubility by the Method
of Back and Steenberg. The values for K_a, K_{sp}, and S for rube-
anic acid were re-determined experimentally. An accurately
weighed portion of rubeanic acid (triple recrystallization from
ethanol) was dissolved in 25.00 ml.0.1N sodium hydroxide by
gentle agitation, without heating. The titration was made imme-
diately after solution was complete, since dithiooxamide under-
goes gradual decomposition in alkaline solutions. The potentio-
metric back titration of the basic solution was made rapidly,
and pH values were measured with a Beckman Model G pH-meter,
carefully standardized with a buffer solution of pH 7.00. The
constants were determined at different ionic strengths (varied
with KCl) and these results are summarized in the accompanying
table.

Table 2. Results by the Back and Steenberg method.

Calculated Quantity	Ionic Strength		
	0.01	0.1	1.0
*K_a	6.54×10^{-11}	5.61×10^{-11}	6.80×10^{-11}
+K_{sp}	2.54×10^{-13}	2.25×10^{-13}	2.84×10^{-13}
S(in moles/liter)	3.88×10^{-3}	4.02×10^{-3}	4.17×10^{-3}

*Average value for K_a based on four determinations.
+Mean value for K_{sp} from two determinations.

Direct Determination of Molar Solubility as a Function of
Ionic Strength. Since the values obtained by the Back and
Steenberg method for K_a, K_{sp}, and S differed significantly from
those reported previously in the literature, it seemed advisable
to check these results by using a direct method to determine the
molar solubility. Determination of solubility by evaporating
to dryness a suitable aliquot from a saturated solution and
weighing the residue did not appear to offer the accuracy required
for application to very slightly soluble compounds, such as dithio-
oxamide. A more sensitive spectrophotometric method was used to
measure the concentration of dithiooxamide in a saturated solu-
tion. Beer's law plots were prepared for rubeanic acid in 1:1
ethanol solutions in the region of the 320 mu band peak. A linear
relationship between optical density and concentration was found
for wave lengths of 390 mu or greater in the concentration range
1.0×10^{-4} to 2.0×10^{-3} molar.

The following experimental method was used in this direct
determination of the molar solubility of rubeanic acid: Fifty

milligram portions of dithiooxamide (triply recrystallized from
ethanol) were placed in each of eight glass-stoppered graduate
cylinders and 50 ml. of distilled water added. The cylinders
were shaken for seven days on a mechanical shaker. At the end
of this interval they were thermostated at 25.0° ± 0.1° C. for
sixteen hours, and 25.00 ml. aliquots were pipetted out, using
a pipet having a fine porosity filter-stick attached to the tip.
The 25 ml. portions were placed in 50 ml. volumetric flasks and
diluted to volume with 95% ethanol. The optical density of each
solution was measured at 390 mu, and the concentration was deter-
mined from the Beer's law plot. Solubility was determined as a
function of ionic strength of the system, which was controlled
by adding suitable amounts of potassium chloride.

Table 3. Solubility of dithiooxamide.

Ionic Strength	:	Solubility
0.0010		4.04 ($\pm$0.04) x 10^{-3} moles/liter
0.010		4.18 ($\pm$0.08) x 10^{-3}
0.10		4.40 ($\pm$0.03) x 10^{-3}
0.50		4.68 ($\pm$0.03) x 10^{-3}
1.00		4.84 ($\pm$0.07) x 10^{-3}

The above values for the solubility of dithiooxamide as a
function of ionic strength show the expected behavior of increas-
ing solubility with increasing ionic strength for   1.0. How-
ever, the extent of this effect is not as great as has been re-
ported by Yaffe and Voigt. Although these values do not check

closely with those obtained by the Back and Steenberg method, it would be expected that the above values are more reliable, since the indirect values are derived from the ratio of the calculated constants, K_{sp} and K_a, and contain the cumulative errors in these quantities. The results obtained by this direct determination and those obtained by the Back and Steenberg method are in sufficiently close agreement to justify the conclusion that the values reported by Yaffe and Voigt are in error.

In studies on the applicability of Debye-Huckel theory to solubility behavior, it is customary to plot log K_{sp} vs $\mu^{\frac{1}{2}}$. A plot corresponding to this was made for dithiooxamide (log S^2 vs $\mu^{\frac{1}{2}}$). Approximate linearity was obtained using S^2, and the slope of the curve lends support to the view that the predominant ionic species in solution is the monobasic acid,

$$
\begin{array}{ccccc}
S~S & & S~SH & & S~S(-) \\
\| ~\| & & \| ~| & & \| ~| \\
H_2N\text{-}C\text{-}C\text{-}NH_2 \rightleftarrows & H_2N\text{-}C~\text{-}C~\text{-}C~ = NH \rightleftarrows & H_2N\text{-}C\text{-}C~ = NH + H^+\text{.}
\end{array}
$$
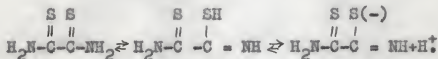
The departure of the point for $\mu=1.0$ from the linear curve would be expected, since the relation of log K_{sp} to $\mu^{\frac{1}{2}}$ is not valid for electrolyte concentrations this great. The linear portion of the curve in Plate I indicates the general validity of the Debye-Huckel prediction.

Equilibria In Dimethylformamide and Methanol

In aqueous solutions dithiooxamide has insufficient acid strength to permit a completely quantitative study of its ionic equilibria. The results obtained using the Back and Steenberg

EXPLANATION OF PLATE I

Fig. 1a. A Beer's law plot of dithiooxamide in ethanol.

Fig. 1b. A plot showing the relationship of solubility
of dithiooxamide to the ionic strength of the
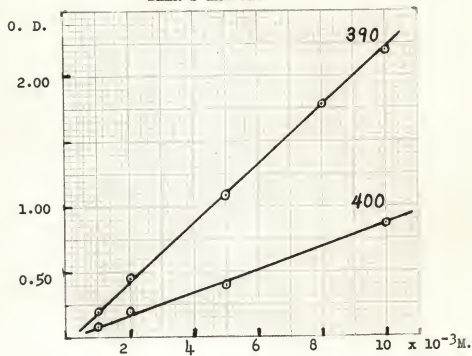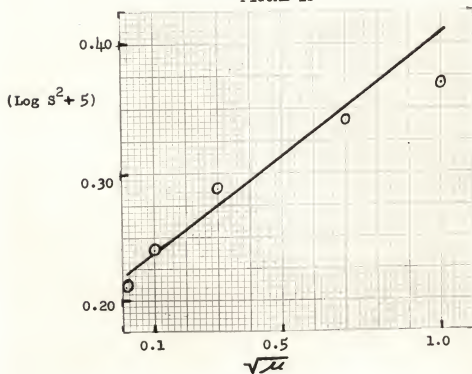solution.

PLATE I
FIGURE 1a
BEER'S LAW PLOT

FIGURE 1b

method demonstrated the very weak nature of the monobasic ioni-
zation of rubeanic acid, and could yield no information on the
dissociation as a dibasic acid. Since experimental evidence
suggests that in the formation of metal rubeanates it may be the
divalent rubeanate anion which reacts with the metal, it was
desirable to obtain direct identification of the various ionic
species in equilibrium in dithiooxamide solutions. It was the
purpose of this portion of this investigation to seek an experi-
mentally sound basis for the theoretically probable mechanism of
acidic dissociation of dithiooxamide.

Although rubeanic acid is too weak to be titrated in aqueous
solutions, Fritz (13), in investigating the nonaqueous titration
of enols and imides, titrated this compound in dimethylformamide
as the solvent with sodium methylate, Azo Violet serving as the
visual indicator. In a basic solvent, such as dimethylformamide,
the strength of weakly acidic compounds is greatly increased.
Therefore, it seemed worth while to compare the acidic behavior
of dithiooxamide in a basic solvent with that in water-like al-
coholic solvents. The results of this investigation are derived
from two experimental approaches. These are: (1) the potentio-
metric titration of rubeanic acid in dimethylformamide solutions
with sodium methylate; (2) and study of the near ultra-violet
absorption spectrum of rubeanic acid alone and in the presence
of base in the solvents, dimethylformamide and methanol.

Experimental Details. Reagents and Solutions. All re-
agents are analytical reagent grade unless otherwise specified.

> Benzene
> Methanol, absolute
> Dimethylformamide, technical (duPont)
> Benzoic Acid, primary standard
> Dithiooxamide (Eastman Organic Chemicals)
> Sodium Methylate (0.1N) standard solution
> Dithiooxamide stock solutions

Six grams of sodium metal were dissolved in 150 ml. methanol
in a flask protected from carbon dioxide. After solution was
complete, 150 ml. more methanol and 1500 ml. benzene were added.
This solution of sodium methylate was stored in a borosilicate
glass bottle, and when used in titrations, the solution was
protected from atmospheric carbon dioxide and moisture. Standardi-
zation was made using primary standard benzoic acid dissolved in
dimethylformamide, titrated potentiometrically.

A 0.3 g. portion of dithiooxamide, accurately weighed, was
dissolved in absolute methanol and diluted to 200 ml. An identi-
cal stock solution of dithiooxamide in dimethylformamide was pre-
pared. Solutions used in spectra measurements were prepared by
transferring appropriate aliquots from the stock solutions to
100 ml. volumetric flasks and diluting to volume with the solvent.

Apparatus and Methods. The Beckman Model DU spectrophotome-
ter equipped with the tungsten lamp was used for all measurements
of absorption spectra. Borosilicate glass cells, having 1 cm.

light path length were used.

For potentiometric titrations in dimethylformamide, a
Beckman Model H pH-meter, which had the calomel electrode re-
placed by an antimony electrode, was used. The titration vessel
was a 250 ml. beaker, covered with a large stopper having openings
for the two electrodes, the burette tip, and a mechanical stirrer.
In actual titrations, the sample of rubeanic acid or benzoic acid
was added to 100 ml. of a solution of 20 percent benzene in
dimethylformamide, in the titration vessel.

Results and Discussion. Potentiometric Titration. It was
verified experimentally that dithiooxamide titrates as a mono-
basic acid in dimethylformamide. In a series of potentiometric
titrations, it was found that in dimethylformamide stable e.m.f.
readings could not be obtained, for there was a steady drift of
the e.m.f. toward higher numerical values. However, by adding
benzene to the system, the tendency of the potential to drift
was completely eliminated. Benzene also had the effect of flatten-
ing the portion of the titration curve immediately preceeding the
break. The magnitude of the break in the titration curve for
dithiooxamide with sodium methylate is not great in dimethyl-
formamide, (only 100 mv.) suggesting that dithiooxamide is still
a weak acid in this solvent. The two potentially titratable
hydrogens are not titrated simultaneously, for the equivalent
weight is equal to the formula weight. In the region of the
break in the titration curve, the red-orange color of rubeanic
acid in dimethylformamide gradually changes to a yellow-orange
color.

It has been assumed in the standardization of sodium methylate with benzoic acid that the latter is a strong acid in dimethylformamide, although direct evidence to support this is lacking, since the titration is usually carried out in benzene-methanol. In dimethylformamide alone it was observed that the magnitude of the break in the titration curve for benzoic acid with base was about the same as that for dithiooxamide. However, when benzene was added to the system the magnitude of the break became much greater and the neutralization was accompanied by the precipitation of sodium benzoate, as occurs in benzene-methanol solvent. It is apparent that in the presence of benzene the overall magnitude of the break in the titration curve is due to the acid-base reaction and the precipitation of the salt.

When the titrations were repeated using re-distilled dimethylformamide (boiling range 150-2° C.), there was no change in the titration curves or in the foregoing observations.

Absorption Spectra. The absorption spectrum of dithiooxamide in dimethylformamide and methanol solutions was determined in the near ultra-violet and visible regions, 320 to 500 mu. Spectral measurements were made on some solutions containing known amounts of sodium methylate, which contained benzene. Since benzene absorbs strongly in the region below 315 mu, measurements were not extended to wavelengths lower than 320 mu. The range of concentrations of dithiooxamide solutions used in all of this work was 1.25×10^{-3} to 1.25×10^{-4} molar.

In the spectrum determined as a function of concentration

of dithiooxamide in dimethylformamide (Plate II), it is noted
that there are two closely overlapping bands, having peaks at
324 and 350 mu. While maintaining a fixed concentration of
dithiooxamide at 1.25×10^{-3} molar, sodium methylate was added
in amounts from zero to eight times the concentration of dithio-
oxamide, and the spectra obtained for these solutions are repro-
duced in Plate II. Here it is observed that immediately upon
the addition of any base to the acid a new band begins to appear,
having a peak at 380 mu, and this new band increases in height,
then decreases as still more base is added. As the new band
appears at 380 mu on the addition of base, there is a corres-
pondingly rapid decrease in the height of the 350 mu band present
initially, until it is no longer detectable. The 324 mu band
remains largely uninfluenced by the addition of base. For amounts
of added base in the range of one to two times the concentration
of dithiooxamide, the height of the 380 mu band remained largely
constant; consequently, while maintaining a constant ratio of
sodium methylate to dithiooxamide of 2:1, the spectrum was deter-
mined for concentrations of 10^{-3} to 10^{-4} molar in dithiooxamide.
These results are represented by the curves in Plate II. It was
found that the height of the 380 mu band decreases with concen-
tration, as does the 324 mu band, and there is no re-appearance
of the 350 mu band.

Similar experiments were carried out using solutions of
dithiooxamide in methanol. The spectrum was measured at dithio-
oxamide concentrations over the same range as was used in di-

EXPLANATION OF PLATE II

The changes in the absorption spectra of dithiooxamide in the presence of sodium methylate (base) in dimethylformamide.

Fig. 2. Dithiooxamide in the absence of base.

Fig. 3a and 3b. Changes in the spectrum produced by sodium methylate.

Fig. 4. The effect of concentration of dithiooxamide on the spectrum in the presence of a two-fold excess of base.

Fig. 5. Dithiooxamide in methanol in the presence of base.

Fig. 6. A plot of absorbancy as a function of concentration of dithio-oxamide in dimethylformamide.

PLATE II

Figure 2   Figure 3a   Figure 3b

Figure 4   Figure 5   Fig.6
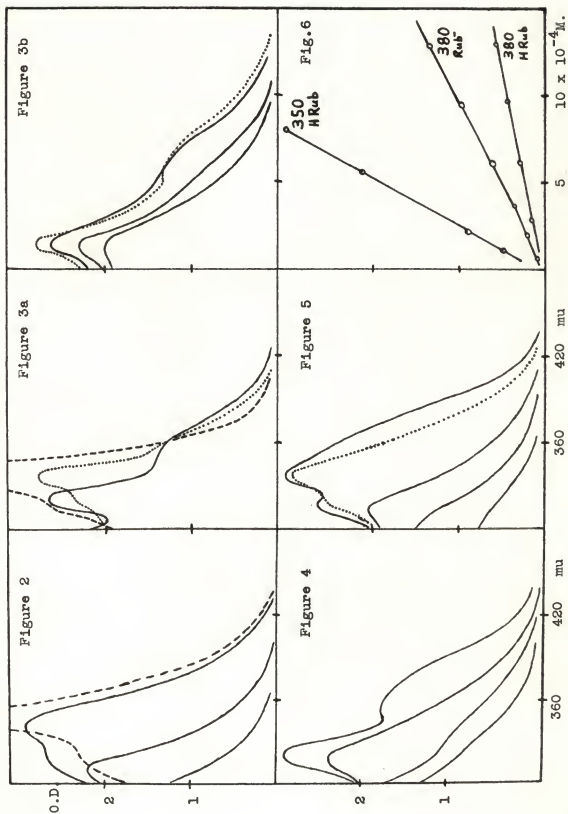
methylformamide. In methanol the same general band structure
was found (Plate II). Band peaks at about 325 and 345 mu were
found at higher concentrations, and as concentration decreased,
the 345 mu band decreased the more rapidly in magnitude. How-
ever, in contrast to dimethylformamide solutions, when 1.25 x
10^{-3} molar dithiooxamide in methanol was treated with various
amounts of base and the spectra determined, it was observed that
there is no apparent effect of base upon the spectrum of dithio-
oxamide for ratios of sodium methylate to dithiooxamide up to 8
to 1. No new band appeared nor did the height (relative or
absolute) of the 325 and 345 bands change on the addition of
base.

Some of the above data were represented in a more convenient
form by plotting optical density vs concentration of dithiooxa-
mide, in Plate II. In dimethylformamide solutions it is noted
that at 350 and 380 mu a Beer's law relationship exists in the
absence of base; in the presence of base an approximately linear
relationship exists for the 380 mu band. For corresponding con-
centrations of dithiooxamide in methanol, Beer's law is applicable
at 380 mu.

The influence of base upon the spectrum of dithiooxamide in
dimethylformamide is shown in a different form in Plate III.
Here optical density in the region of the 350 and 380 mu bands
is plotted against the ratio of sodium methylate to dithiooxamide.
This mole ratio method is preferred for systems involving several
species in solution (24). It is observed that three distinct

inflection points occur at each wavelength used; and that these
points correspond very closely to the ratio 1:2:3 with respect
to base. The fact that the ratio of sodium methylate to dithio-
oxamide does not have a whole number value at the inflection
points is understandable in view of the measurements having been
made on strongly overlapping absorption bands.

The probable molecular and ionic species present in a solu-
tion of dithiooxamide may be represented by the following equili-
bria:

$$(I) \qquad\qquad (II) \qquad\qquad (III)$$
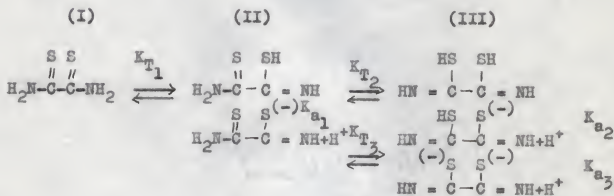
Each of the tautomeric equilibria, when considered alone, are
independent of the hydrogen ion concentration. However, since
tautomeric forms (II) and (III) are mono- and dibasic acids re-
spectively, the relative concentrations of the various tautomeric
forms should be influenced significantly by the removal of hy-
drogen ions. Therefore, for our discussion it will be assumed
that any acidic character of dithiooxamide solutions is attri-
butable to the dissociation of thiol forms (II) or (III), or
both, as acids. If base is added to a solution containing the
above species, the removal of hydrogen ion will be accompanied

by an increase in the concentration of an ionic form, or forms, of dithiooxamide and a decrease in the concentration of one or more of the undissociated forms. Consequently, on the addition of base to the system, the tautomeric equilibria would be expected to shift toward the right.

Changes in the absorption spectrum of dimethylformamide solutions of dithiooxamide which occur upon the addition of base can be interpreted with the help of the equilibria given above. The plot of optical density vs the ratio of base to dithiooxamide (Plate III) is the most informative for representing quantitatively these changes. The three inflection points in the graph indicate an apparent reaction of three moles of base per mole of dithiooxamide. In attempting to identify the 380 mu absorption band with a particular ionic species formed on the addition of base, two possible interpretations which will account for a reaction consuming two equivalents of base are suggested. The first, and probably obvious, mechanism is the stepwise reaction of the base with the tautomeric di-imido form (III). In this case the initial concentration of the ionic form of the dibasic acid is small, and it increases as hydrogen ion is removed by the addition of base, up to the first equivalence point. Then, on the addition of more base the optical density remains essentially constant until the second equivalence point is reached. This is consistent with the expectation that the spectra of the mono- and divalent ions formed by the dissociation of the di-imido form would be identical in this region. And, to support this mechanism, one could argue that, if the 380 mu band were due to the reaction

of base with acidic species (II), the optical density should de-
crease immediately beyond the first equivalence point; otherwise,
in order to account for the horizontal portion of the curve be-
tween the first and second equivalence points, both the ionic
form of (II) and the divalent form of (III) would have to absorb
at the 380 mu band and have practically identical extinction co-
efficients, the latter being somewhat improbable. A second path
that can be suggested to account for the experimental results
plotted in Plate III is that base first reacts with hydrogen
ion from the acid mono-imido form (II) and then the second
equivalent of base reacts with the hydrogen ion formed by the
dissociation of the ionic mono-valent di-imido form (III). In
this case the ion of mono-imido acid increases in concentration
as base is added up to first equivalence point; then, the di-
valent di-imido ion must absorb in the same region and have an
extinction coefficient less, equal to, or greater than the first
ionic species. Equivalent extinction coefficients for the two
ions would be quite improbable. However, the graph indicates
that optical density values between the two equivalence points
do not fall on a horizontal line, but optical density definitely
increases as the second equivalence point is approached. This
same effect is found in plotting values taken from the 350 mu
band as well as the 380 mu band. Even though the contribution
of the 350 mu band to the optical density value decreases as the
amount of added base increases, in the region between the first
and second equivalence points the plot shows an overall increase

EXPLANATION OF PLATE III

Beer's law plots used in calculation of equilibrium constants.

Fig. 7.   Absorbancy as a function of the mole ratio of base to dithiooxamide.

Fig. 7b. Beer's law plot for copper rubeanate, and the determination of copper with diethyldithiocarbamate.

Fig. 8.   Calibration curves used for the determinations of cobalt and nickel. The reagents used were thiocyanate for cobalt and dimethylglioxime for nickel.

PLATE III

Figure 7

Figure 7b
Cu Rubeanate

Cu Diethyldithiocarbamate

Figure 8
Co Determination

Ni Determination
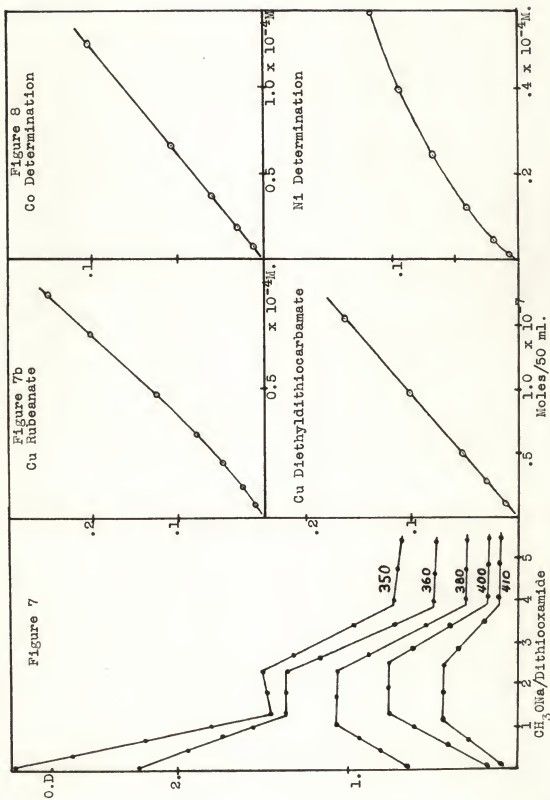
in optical density as more base is added. In the region of the
380 mu band a decrease in the optical density between the first
two equivalence points could be attributed to the decrease in
the contribution due to the overlapping 350 mu band. However,
since optical density neither decreases nor remains constant,
but actually increases significantly between the two points
probides strong evidence for the second interpretation. It is
this latter view which this writer favors.

The predominant absorption band in dimethylformamide solu-
tions of dithiooxamide, having a peak at 350 mu, decreases
rapidly on the addition of base. This would indicate the dis-
appearance of one of the tautomeric forms as the equilibrium
shifts toward an ionic species upon the removal of hydrogen ion
by added base. It seems reasonable to attribute this band to
the dithioamide form (I) in the equilibria given above. This
would be compatible with both of the interpretations given for
the 380 mu band, for as long as appreciable amounts of the di-
thioamide form remained the concentrations of the undissociated
mono- and di-imido forms (II) and (III) would remain unchanged
by the addition of base, and only the dithioamide form would
exhibit an immediate and continuous decrease in concentration
as the hydrogen ion concentration is decreased.

It is noteworthy that absorption spectra of solutions of
dithiooxamide in methanol, an extremely weak acidic solvent,
show no change on the addition of base even when added in con-
siderable excess. From the equilibria (2), one would conclude

that the concentration of hydrogen ion in methanol is exceedingly small and exhibits no measurable reaction with base. The tautomeric equilibrium must favor almost completely the dithioamide form (I).

The equilibria outlined above for dimethylformamide solutions of dithiooxamide do not indicate the particular species that is responsible for the consumption of the third equivalent of base as shown in Plate III. However, one would presume that the base reacts with the divalent di-imido ion, either with hydrogen ion or with the divalent ion itself. In an effort to learn more about the consumption of the third equivalent of base by dithiooxamide, and also as a check on the identification of the absorption bands of dithiooxamide in dimethylformamide, the absorption spectrum of the S, S'-dimethyl derivative of dithiooxamide was determined in the same solvent. This particular derivative can not show the two tautomeric forms (I) and (II) of dithiooxamide, but may be considered as a derivative of the unionized form (III). The absorption spectrum of 1×10^{-3} molar solutions in dimethylformamide was determined from 315 to 500 mu. No absorption bands were found at 350 to 380 mu, nor were any band peaks found in this wavelength region. However, from 315 to 340 mu, the declining portion of an absorption band whose peak is farther in the ultra-violet was observed. This absorption band was found to be unstable with respect to base, for, on the addition of sodium methylate to solutions of the derivative, the optical density decreased rapidly to almost zero in a few minutes. (The ratio of base to derivative in this case ranged from 0 to 2.) Although

this evidence of S, S'-dimethyldithiooxamide indicates that base can react with the di-imido form of dithiooxamide, it has not been determined how the reaction occurs. Nevertheless, these observations of the S, S' derivative are consistent with the interpretation of the absorption spectrum of dithiooxamide in dimethylformamide.

Determination of the Extinction Coefficients for Band Peaks. From the dilution experiments in dimethylformamide for dithiooxamide with no base present, an approximate Beer's law relationship is obtained for the peak at 350 mu. This band was identified with structure (I), abbreviated RSRS. Likewise, an approximate Beer's law plot is obtained for the momobasic acid species, RSRS$^-$, at 380 mu for solutions having dithiooxamide to sodium methylate mole ratio of 1:2. The extinction coefficient for the 350 mu band can be calculated directly. Since the 380 mu band is not well resolved, the molar extinction coefficient can not be calculated in the same manner. However, if one determines the ratio of the optical densities at the same concentration on the two band peaks for these two colored species, one obtains the ratio of their molar extinction coefficients, since

$$\log \frac{I_{o_1}}{I_1} = e, c, d \text{ and } \log \frac{I_{o_2}}{I_2} = e_2 c_2 d.$$

If $C_1 = C_2$

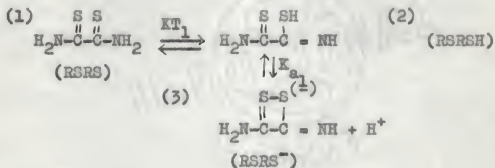$$\frac{\log \frac{I_{o_1}}{I_1}}{\log \frac{I_{o_2}}{I_2}} = \frac{e_1}{e_2}$$

In Table 4, calculated values for the molar extinction coefficients are given.

Table 4. Molar extinction coefficients.

Conc.	O.D.: 350mu:	O.D.: 380mu:	e_{350}/e_{380}	$e_{350}(\log 10)$	$e_{380}(\log 10)$
1.2×10^{-4} M.	0.362	0.80	4.53	3620	745±50
2.4×10^{-4}	0.670	0.150	4.47	3350	
4.2×10^{-4}	1.295	0.281	4.61	3240	
6.4×10^{-4}	1.91	0.425	4.50	3180	
8.4×10^{-4}	2.54	0.620	4.10	3180	
			Av. 4.44 (±0.14)	Av. 3.31×10^3 (±0.14 x 10^3)	

Since the absorption bands are not well resolved, but overlap strongly, it should be borne in mind that the constants calculated for the various equilibria involved will be approximate values only.

It is possible to calculate, directly, constants for the following equilibria, using data from the various absorption spectra.

(1)
$$\underset{(RSRS)}{H_2N-\overset{S}{\overset{\|}{C}}-\overset{S}{\overset{\|}{C}}-NH_2} \overset{KT_1}{\rightleftharpoons} \underset{(RSRSH)}{H_2N-\overset{S}{\overset{\|}{C}}-\overset{SH}{\overset{|}{C}} = NH} \quad (2) \quad (RSRSH)$$

$$(3) \quad \uparrow\downarrow K_{a_1}^{(\pm)}$$

$$\underset{(RSRS^-)}{H_2N-\overset{S-S}{\overset{\|\ \ |}{C}-C} = NH + H^+}$$

From the qualitative discussion on the spectra, it was concluded

that in the absence of added base, the predominant species in the
system is (1), which for convenience will be appreviated as RSRS.
Stated in another way, K_T for this tautomeric change will be
less than unity. Species (2) may be abbreviated as RSRSH and
(3) as RSRS⁻. The following equilibrium relationships are
applicable:

$$K_{T_1} = \frac{(RSRSH)}{(RSRS)} \quad ; \quad K_{a_1} = \frac{(RSRS^-)(H^+)}{(RSRSH)}$$

For the case in which base (sodium methylate has been added to
the system in an amount less than that required to reach the
first equivalence point, the changes in the absorption spectrum
have been attributed to increases in the concentration of RSRSH
and RSRS⁻. Using the Beer's law plot for the band peak at 380
mu, one can determine the concentration of these two species
(RSRSH + RSRS⁻). The concentration of base added will be equiva-
lent to the concentration of RSRS⁻ formed by the titration of the
corresponding amount of hydrogen ion. Let the total analytical
concentration of dithiooxamide added be represented by C_R. Then
it follows that

$$C_R = (RSRS) + (RSRSH) + (RSRS^-)$$
$$= (RSRS) + (RSRSH) + (H^+)$$
$$(RSRS) = C_R - (RSRSH) + (RSRS^-)$$
$$(H^+) = C_R - (RSRS) + (RSRSH) .$$

Initially, in the
absence of added
base (RSRS⁻)=(H⁺)

$$K_{T_1} = \frac{(RSRS^-)(H^+)}{K_{a_1}(RSRS)}$$

For mixtures of dithiooxamide and sodium methylate in dimethyl-
formamide solutions, the quantities known experimentally are

Concentration of CH_3ONa = $(RSRS^-)$

Concentration (total), dithiooxamide = C_R

Concentration of $RSRSH + RSRS^-$ from 380 mu band, and
the quantities calculated are (H^+), $(RSRS)$, $(RSRSH)$ and K_a. The
value of K_{T_1} may be calculated from the relation to K_{a_1} above,
or it may be evaluated graphically by plotting the ratio $\frac{(RSRSH)}{(RSRS)}$
against CH_3ONa concentration, and the y-intercept becomes equal
to K_{T_1} when CH_3ONa becomes zero. The graphical method is pre-
ferable, since the errors in the calculation of K_{a_1} are also
added to the calculated value of K_{T_1}.

From the equilibria in the system, as base is added to a
fixed concentration of dithiooxamide, the concentration of RSRS
will decrease and $RSRS^-$ will increase by the corresponding
amount. However, the concentration of RSRSH will remain essen-
tially constant until no more RSRS remains, which will occur in
the immediate vicinity of the first equivalence point. The con-
centration of RSRSH can be calculated indirectly from the Beer's
law plots. For a given concentration of base, the optical density
at 380 mu represents $(RSRSH + RSRS^-)$. In the absence of base, it
would be expected that RSRSH would be present in the larger con-
centration, and the increase in optical density value in the addi-
tion of base would represent the increase in $RSRS^-$ concentration.
Then the difference between the optical density in the presence

of base and that with no base added will be equivalent to the
amount of dithiooxamide that would have to be added to achieve
the same optical density. Assuming that the concentration of
base is nearly equivalent to RSRS⁻, then the difference between
this concentration of dithiooxamide (presumed to be largely
RSRS) and (RSRS⁻) is approximately equal to the concentration
of RSRSH, or

$$(RSRS^-) - (RSRS) \text{ difference} = (RSRSH).$$
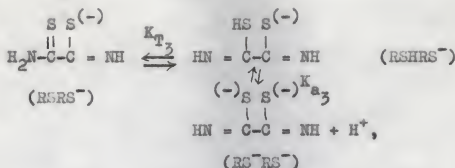
The calculation of (H^+) must, likewise, be made indirectly.
On the addition of base it has been assumed that the concentra-
tion of CH_3ONa is approximately equivalent to RSRS⁻ formed by
the titration of hydrogen ion. For a given case, the optical
density measured at 380 mu actually measures the sum of the
concentrations of RSRS⁻ present initially in the absence of
added base (and equivalent to the hydrogen ion concentration),
the amount of undissociated RSRSH (if it absorbs at this wave
length), and RSRS⁻ formed by the addition of an equivalent
amount of base. Or, this may be represented by an equation,

$$(RSRS^-)_{diss.} + (RSRSH) + (RSRS^-)CH_3ONa = \text{Total concn. deterd.}$$
at 380 mu.

where $(RSRS^-)_{diss.} = (H^+)$, $(RSRS^-)CH_3ONa = RSRS^-$ formed equiva-
lent to base added. As was noted above, the concentration of
RSRSH is largely constant in the presence of added base over the
range considered here. If RSRSH absorbs significantly at 380 mu,
the difference between $(RSRS^-)_{CH_3ONa}$ and the sum of the above

adsorbing species must exceed the concentration of RSRSH previous-
ly calculated; and this difference would be equivalent to the sum
of (RSRSH) and $(RSRS^-)_{diss}$. From actual numerical calculation,
it was found that this difference was less than the calculated
concentration of RSRSH, suggesting the conclusion that RSRSH
does not absorb at this wave length. Therefore, the difference
is now equal to $(RSRS^-)_{diss}$, which is equivalent to (H^+). This
value for (H^+) was used to calculate K_{a_1}.

From the plot of optical density vs CH_3ONa/dithiooxamide
ratio (Plate III), it appears that beyond the first equivalence
point the concentration of $RSRS^-$ decreases and a second absorbing
species forms as the second equivalence point is approached; then
the latter decreases on the addition of more base. In the inter-
val between the first and second equivalence points, the major
species, initially, is $RSRS^-$, which will be the starting point
for the second tautomeric change. Consequently, from the absorp-
tion spectra one would expect that only K_{T_3} and K_{a_3} could be
calculated, using the method for evaluating K_{T_1} and K_{a_1}. The
concentration of $RSRS^-$ can be determined, using the assumption
that C_R is now equivalent to $RSRS^-$ when no base is present in
excess of that required to react with the first titratable hy-
drogen. For this case, the portion of the equilibrium to be
considered is simplified to

$$H_2N-\overset{\overset{S}{||}}{C}-\overset{\overset{S}{|}}{C} = NH \overset{K_{T_3}}{\rightleftharpoons} HN = \overset{\overset{HS}{|}}{C}-\overset{\overset{S}{|}}{C} = NH \qquad (RSHRS^-)$$

$$(RSRS^-) \qquad \qquad \overset{\text{↑↓}}{\underset{(-)\overset{|}{S}}{}}\overset{\overset{S}{|}}{S}^{(-)}K_{a_3}$$

$$HN = \overset{\overset{|}{C}}{C}-\overset{\overset{|}{C}}{C} = NH + H^+,$$

$$(RS^-RS^-)$$

and the applicable relationships are

$$K_{T_3} = \frac{(RSHRS^-)}{(RSRS^-)} \; ; \quad K_{a_3} = \frac{(RS^-RS^-)(H^+)}{(RSHRS^-)}$$

using the optical density value (380 mu band) at the first equivalence point to determine the actual concentration of $RSRS^-$, and assuming the concentration of RS^-RS^- to be small compared to $RSHRS^-$ (there is potentiometric evidence for K_{a_3} being very small), the difference

$$C_R - (RSRS^-) \simeq (RSHRS^-).$$

Then an approximate value for K_{T_3} can be calculated.

In attempting to calculate K_{a_3}, the following quantities are known: approximate value for $RSRS^-$ from O.D. near first equivalence point; $(RS^-RS^-) \simeq$ concn. CH_3ONa added beyond first equivalence point; $C_R = (RSRS^-) + (RSHRS^-) + (RS^-RS^-)$; remaining titratable hydrogen $= (RSRS^-) + (H^+) + (RSHRS^-)$. However, there is no information that can give a value for the concentration of RS^-RS^- due to the dissociation of the acid in the absence of added base, nor can a value for (H^+) be determined. Approximations of the type used to evaluate the corresponding

quantities in the calculation of K_{a_1} are not valid for this case, since K_{a_3} is small and also two colored species are absorbing strongly in this 380 mu region. Consequently, no calculation of K_{a_3} could be made from this approach. Likewise, calculation of K_{a_3} from relationships between K_{T_1}, K_a, K_{T_3}, and K_{a_3} can not be made without knowing the concentration of (H^+) or (RS^-RS^-).

The numerical values for the various quantities that were calculated as outlined above, are summarized in the accompanying Table 5. The value for K_{a_1} in dimethylformamide is about 10^7 times greater than in aqueous media. Since there is no evidence

Table 5. Data used in calculations.

Total Dithiooxamide conc. C_R 1.25 x 10^{-3} molar			
Sodium Methylate :	RSRSH :	(H^+) :	RSRSH/RSRS
2.2 x 10^{-4} M.	3.4 x 10^{-4} M.	5.7 x 10^{-4}	0.74
4.4 x 10^{-4}	3.3 x 10^{-4}	3.6 x 10^{-4}	0.73
6.05 x 10^{-4}	3.1 x 10^{-4}	2.9 x 10^{-4}	0.885
8.8 x 10^{-4}	3.2 x 10^{-4}	1.1 x 10^{-4}	1.23
9.9 x 10^{-4}	2.6 x 10^{-4}	0.9 x 10^{-4}	1.53

for the existence of the undissociated diimido form (III), K_{T_2} and K_{a_2} are imaginary. The computed values for the constants K_{T_1}, K_{a_1}, and K_{T_3} are given in Table 6.

Table 6. Computed values for equilibrium constants.

K_{T_1}	:	K_{a_1}	:	K_{T_3} (approximate)
0.74		3.79×10^{-4}		0.0204
		4.4×10^{-4}		
		5.75×10^{-4}		
		3.02×10^{-4}		
		3.43×10^{-4}		
		Av. 4.1×10^{-4} ($\pm 0.7 \times 10^{-4}$)		

As was noted earlier, the maximum concentration of the rubeanate ion will be obtained in alkaline solution, but over a one hour interval in such media significant decomposition is observed from the decline in the 324 and 350 mu bands with time. Consequently, analytical determinations using rubeanic acid in alkaline media are to be avoided, since the metallic ions may well yield insoluble products by reaction with sulfur-containing decomposition products of the reagent. The mechanism and products of the decomposition of dithiooxamide were not experimentally investigated; however, some deductions can be made from studies reported for closely related thioamides and thiols. One of the final products of decomposition of disulfides, thiols, and thio-amides is hydrogen sulfide (10, 14, 30). It is produced by the action of heat, ultraviolet light, and strong acids and bases, but the route whereby it is formed is dependent on the type of thiofunctional group and the agent. Thioacetamide is related structurally to dithiooxamide, and its hydrolysis in acid and alkaline media is a familiar method for producing hydrogen sulfide.

The mechanism and kinetics of this hydrolysis have been studied recently by Rosenthal and Taylor (30). Changes in the U. V. absorption spectrum of thioacetamide with added acid and base lead to the identification of thioacetic acid as an intermediate in the hydrolysis, but their assignment of one band to protonated thioacetamide is not necessarily correct. The decomposition of thiourea in water solution yields thiocyanic acid, but lacks the significant pH dependence that the thioacetamide hydrolysis shows (32). All of these decomposition products will form precipitates with most of the metals with which rubeanate ion reacts.

REACTION OF DITHIOOXAMIDE WITH METALLIC IONS

The reaction of rubeanic acid with three typical metals in their plus two oxidation states was studied. The water insoluble rubeanates of copper, cobalt, and nickel were isolated and empirical formulae determined by elemental analysis. Quantitatively measured values for the molar solubilities of these compounds were used to calculate solubility product constants. From this information, as well as from solubility behavior in organic solvents and from molecular models, it is possible to deduce reasonable structures for the metal rubeanates.

Copper Rubeanate

Qualitative Solubility in Various Organic Solvents: The most widely used analytical application of dithiooxamide is the colorimetric determination of copper. In such procedures the dark green colored copper rubeanate is formed in a buffered solution at pH 4,

and the system is stabilized by the addition of gum arabic to prevent the precipitation of very insoluble copper rubeanate. Since it has been observed that for wide ranges of copper concentrations the Beer's law plot departs from linearity, it seemed important to determine if water miscible or immiscible solvents could be found in which copper rubeanate is completely soluble.

The method of preparation of copper rubeanate is based upon the analytical procedure of Willard, Mosher, and Boyle (44) with the only change being that gum arabic is omitted. The following materials were used:

Copper Standard--0.1 mg Cu/ml, as $CuSO_4 \cdot 5H_2O$

Buffer pH 4 -- 40 g. ammonium acetate dissolved in 20 ml. water, then 40 ml. glacial acetic acid added, dil. to 1000 ml.

Dithiooxamide --0.01 molar in 95% ethanol.

Acetone

amyl alcohol

n-butanol

dimethylformamide

dioxane

ethanol

ethylacetate

mesityl oxide

petroleum ether

benzene

xylene

One ml. of copper standard and 1 ml. of buffer was placed in a tube and iluted to 10 ml. An equal volume of solvent was added if water-miscible; if immiscible, 5 ml. are added. Add 1 ml. of dithiooxamide and mix.

A series of experiments were made, using two added solvents.

(1) Chloroform (5 ml.) and 0.5,1,2,5, 10 ml. dioxane. All gave a green-black color in chloroform and a green-black precipitate in the aqueous phase.

(2) n-Butanol (3 ml.) and 0.1, 0.2, 0.5, and 1 ml. dioxane (a homogeneous mixture). The first three had a green-color and precipitate in butanol phase, while 1 ml dioxane was clear, green-black solution and a slight precipitate in 30 minutes with no fading.

(3) Isopropanol (5 ml.) and 0.1, 0.5, 1, 2, and 5 ml. dioxane. Clear green-black color and after 30 minutes a slight precipitate but no significant fading.

(4) Ethanol (3 ml.) and 0.1, 0.2, 0.5, and 1 ml. dioxane. Clear, green-black solution, but precipitate in 30 minutes.

(5) Dimethylformamide (5 ml.) and 0.1, 0.2, 0.5, 1, and 2 ml. butanol (homogeneous solution in all cases). Green-black clear solutions, but precipitate in 30 minutes.

(6) Dimethylformamide (5 ml.) and 0.1, 0.2, 0.5, and 1 ml. dioxane. Green-black clear solution, but precipitate in 30 minutes.

In general the addition of an immiscible solvent resulted in immediate gross precipitation of copper rubeanate at the interface between the two liquids. Isopropanol-water and dioxane-water were the most satisfactory in giving clear solutions immediately. However, a small amount of precipitate formed at the liquid-air interface in 30 minutes. The addition of a second organic solvent to these systems did not prevent this precipitation on standing. The color intensities of the water-isopropanol

and water-dioxane solutions of copper rubeanate were less than
the intensity of the corresponding water solution stabilized
with gum arabic. Therefore, in the detection of small concen-
trations of copper the addition of an organic solvent in place
of gum arabic offers no advantage and is less sensitive than
the original method.

A Beer's law plot (Plate III) was prepared for copper ru-
beanate in aqueous solution containing gum arabic. The concen-
tration range of copper rubeanate was 5.0×10^{-6} to 1.0×10^{-4}
molar. At the lower concentrations it was observed that there
was a slight departure from a straight line relationship; however,
as a curve for the quantitative determination of copper or the
detection of copper rubeanate in solution, this slight departure
from linearity is not important.

Evaluation of the Molar Solubility of Copper Rubeanate in
Aqueous Solution. An investigation was made to determine quanti-
tatively the molar solubility of copper rubeanate in buffered
solutions from which copper is usually precipitated with rubeanic
acid. The ammonium acetate-acetic acid buffer maintains the pH
between 4 and 5 and the ionic strength of the system is about
0.02. It was found that the level of copper rubeanate in a
saturated solution was too low to be detected by direct spectro-
photometric measurement at 650 mu, the absorption peak of this
compound. Consequently, a suitable method for concentrating
the soluble copper in a saturated solution had to be developed.

It was thought that a colorimetric reagent for copper, having

an instability constant less than copper rubeanate and one form-
ing a copper chelate that is soluble in an immiscible solvent,
could serve as a simple method for concentrating and determining
the soluble copper in one step. Since sodium diethyldithiocar-
bamate is one of the most sensitive reagents for copper and readi-
ly extracts the metal into carbon tetrachloride, this reagent was
added to a portion of a saturated solution of copper rubeanate
and the extraction made. This method was not suitably sensitive
for the detection of copper in this solution, and this general
approach to the problem was discontinued.

The following procedure was successfully applied to the
determination of the solubility of copper rubeanate.

Copper rubeanate was precipitated in an aqueous ammonium
acetate-acetic acid buffer solution, pH 4.60, with dithiooxamide.
A duplicate solution containing no added copper other than from
the reagents themselves was prepared simultaneously to serve as
a complete reagent blank. After allowing these solutions to
stand one week, they were thermostated at 25.0+0.1°C. and 50.00
ml. aliquots withdrawn through a filter stick. These aliquots
were evaporated to 20 ml., 1 ml. of HNO_3 and 2 ml. H_2SO_4 were
added to destroy the organic matter and the solution was evaporated
to dense fumes of SO_3 (about 2 ml. volume). After cooling to room
temperature, the residues were dissolved in 20 ml. of water, trans-
ferred to small separatory funnels, and the copper content deter-
mined with sodium diethyldithiocarbamate according to the method
of Sandell (31). The experimentally determined Beer's law plot

for low levels of copper is shown in Plate III. The difference
between the copper content of the saturated solution of copper
rubeanate and that of the complete blank carried through all
operations gave a figure for the solubility of copper rubeanate
in this system.

Based upon four determinations by this method, the value
for the molar solubility of copper rubeanate at pH 4.60 and
ionic strength 0.02 is 3.90 ($\pm$0.11) x 10^{-7} moles per liter.

Table 7. Determination of soluble copper.

O.D. Solution:	Concn. Cu. :	O.D. Blank:	Conc. Cu.
0.046		0.028	
0.044		0.027	
0.047		0.026	
0.045		0.028	
Av.0.046	0.470×10^{-7} moles/50 ml.	0.027	0.275×10^{-7} moles/50 ml.

In this determination the value measured represents the total
copper in solution which may be formulated as follows:

$$Cu_{(Total\ Soluble)} = CuRub_{(Soluble)} + Cu^{+2}_{(dissoc.\ from\ CuRub)} + Cu^{+2}_{(unppt'd)}.$$

Usually in treating slightly soluble inorganic compounds, it is
assumed that in the solution phase the dissolved compound is
completely dissociated. For a metal chelate, which in itself
is slightly dissociated, it seems questionable that one should

accept this same assumption without experimental evidence of its
validity or a knowledge of the instability constant for the che-
late. Therefore, this question of the actual meaning of the
solubility value for copper rubeanate as determined above was
investigated.

Approximately one- and one-half grams of copper rubeanate
was prepared and isolated for use in additional solubility ex-
periments. This product was prepared from a solution of 2.5 g.
cupric sulfate, 4 g. of ammonium acetate, 4 ml. of glacial
acetic acid, and 400 ml. water. To this solution, 1.5 g. of
rubeanic acid in 200 ml. ethanol were added, and the mixture
was allowed to stand for twenty-four hours. The precipitate was
filtered off on a fine porosity sintered glass crucible, washed
several times with (1+1) ethanol, absolute ethanol, air dried,
and finally vacuum dried for seventy-two hours. Room temperature
drying was used to avoid possible thermal decomposition at elev-
ated temperatures. Because of the extreme insolubility of copper
rubeanate in all types of polar and nonpolar solvents, it was
impossible to recrystallize this material. Copper rubeanate was
analyzed for copper content, using the standard electro-deposi-
tion method given in Kolthoff and Sandell (19). Two-tenths gram
samples were decomposed with nitric acid, then sulfuric acid, and
heated to dense fumes prior to the deposition of copper. The
analytical results gave a 1.00 to 1.19 ratio between copper and
rubeanic acid in the compound isolated, showing essentially a
1:1 ratio for the reactants. However, it appeared probable that

the product was contaminated with rubeanic acid. X-ray examination demonstrated that the material is finely crystalline and contained no detectable rubeanic acid. It may be that the product contains some water or alcohol of crystallization. The ratio of copper to rubeanate concurs with the findings of Ray and Ray (29). If the data are recomputed, assuming a salt-like composition corresponding to one mole of acetate per mole of copper rubeanate and abbreviated as $Cu(HRub)(CH_3COO)$, a 1.00 to 1.02 ratio is obtained. In view of the comparatively large amounts of acetate present in the buffered precipitation medium, this assumption is not without justification. A spot test (12) indicated the presence of significant amounts of acetate in solid copper rubeanate.

Portions of the copper rubeanate prepared above were removed prior to the air drying and were placed in aqueous solutions buffered at pH 4.6 and containing a larger excess of rubeanic acid. The total soluble copper in this system was determined after one week as before. In this experiment it was hoped that by adding a large excess of rubeanic acid and restricting the copper in solution to that coming from the dissolution of copper rubeanate, the value for soluble copper would be nearly equivalent to the concentration of dissolved CuRub if such a species exists. The total ionic copper from the two sources is assumed to be negligibly small. Experimentally, the total copper in solution in this case did not exceed the correction for the reagent blank. Two possible explanations may be suggested: (a) the rate of solu-

tion of solid copper rubeanate is exceedingly slow, with no detectable copper going into solution in one week; or (b) the soluble chelate species $CuRub_{(Soluble)}$ does not exist and the $Cu_{(Total\ Soluble)}$ represents the total ionic copper in the system. The validity of the first explanation was tested by adding a portion of solid copper rubeanate to water alone (no added buffer or excess rubeanic acid) allowing the system to stand one week with shaking and the soluble copper was determined. Very significant amounts of copper were found. In four determinations the total soluble copper was 1.26 ($\pm$0.01) x 10^{-4} moles/l. Thus, it appears that one is justified in assuming the total copper in solution is in the form of ionic copper, or small polymers of the rubeanate.

Since the amount of ionic copper in solution in equilibrium with the solid copper rubeanate is known, it would seem practical to calculate the solubility product. However, if copper (II) reacts only with the doubly charged anionic rubeanate, and we have no method for evaluating the concentration of Rub^{-2} or the second dissociation constant for rubeanic acid, the actual solubility product for copper rubeanate can not be calculated with the present information. Only by the assumption that the copper rubeanate has the composition suggested above and using the first acid dissociation constant for rubeanic acid to calculate the concentration of the singly charged rubeanate ion, can one compute a maximal value for K_{sp}.
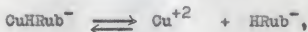
For the dissociation of rubeanic acid in aqueous solution, we know that

$$H \, rub \rightleftharpoons H^+ + Rub^-$$

and $\quad K_{a_1} = \dfrac{(H^+)(Rub^-)}{(H_2Rub)} \qquad 6.54 \times 10^{-11}$ at $\mu = 0.012$

Experimental evidence indicates that

$$CuHRub^- \rightleftharpoons Cu^{+2} + HRub^-,$$

and substituting $HRub^-$, we find

$$K_{sp} = (Cu^{+2})(HRub^-) = \frac{(Cu^{+2})(H_2Rub) \, Ka_1}{(H^+)}.$$

Using known numerical values of pH = 4.60, $(Cu^{+2}) = 3.90 \times 10^{-7}$ M., and $(HRub^-) = 5.0 \times 10^{-7}$ M., the calculated value for K_{sp} was found to be $5.08 \pm 0.08 \times 10^{-16}$ at an ionic strength of 0.02.

Cobalt and Nickel Rubeanates

The rubeanates of cobalt and nickel are not formed nor precipitated in acidic media at the 20 to 100 p.p.m. level. Consequently, all experiments on the formation of these compounds were made in buffered media at pH 7.0. As in the case of copper rubeanate, systems involving low levels of nickel and cobalt with rubeanic acid can be stabilized by the addition of gum arabic to prevent precipitation, if this is desired.

Solubility in Organic Solvents. A qualitative study on the solubility of the rubeanates of cobalt and nickel in various

organic solvents was made, using the same method as outlined for copper rubeanate. The only modifications were: (1) the standard nickel and cobalt solutions were 3×10^{-4} M., and (2) one ml. of pH 7.0 buffer solution was used. The same solvents used for the solubility experiments on copper rubeanate were used here as well.

The rubeanates of cobalt and nickel behaved similarly. In general these were not extracted into water-immiscible solvents, but precipitation occurred at the water-solvent interface. A slight amount of the purple nickel rubeanate was extracted into n-butanol; however, upon doubling the amount of nickel ion present in the aqueous phase, no additional color was extracted, but the precipitate formed at the interface. For water-miscible solvents, a haze of the metal rubeanate was formed that was equal to or greater than that produced in water containing no organic solvent. The only exception was the formation of cobalt rubeanate in 50 percent dioxane, in which the yellow color developed without the appearance of a turbidity in less than thirty minutes. Measurements of concentration as a function of absorbancy at the 420 mu maxima of cobalt rubeanate were made on such dioxane-water solutions. However, the data were quite non-reproducible, showing a strong time dependency, and at concentrations above 10^{-5} M. precipitation occurred. The first two effects were traced to a reaction between dioxane and rubeanic acid, yielding a steadily increasing yellow color in the absence, as well as in the presence, of cobalt.

Quantitative Determination of the Solubility of Cobalt, and
Nickel, Rubeanates. The molar solubilities of the rubeanates of
cobalt and nickel were determined in solutions buffered at pH
7.00 and at ionic strength of 0.02. The method used follows.

Ten ml. of 3×10^{-4} M. standard solution of the metal ion
and 10 ml. of buffer solution were placed in a flask and diluted
to 40 ml.; 1.5 ml. of 10^{-2} M. dithiooxamide (in ethanol) was
added and the mixture diluted to a final volume of 50 ml. The
stoppered flask was allowed to stand three days, and the preci-
pitate was filtered off, washed six times, and transferred to a
new flask containing 50 ml. of buffer and diluted to a volume of
250 ml. (In this way the aqueous phase contains no excess reagents
or alcohol.) The flask was then shaken for three days in a constant
temperature bath at $25.0 \pm 0.2°C$. prior to determining the solubil-
ity. After this interval, the contents of the flask was filtered
through an ultra-fine sintered glass filter, and a 100.0 ml.
aliquot of the filtrate was transferred to a beaker, 2 ml. of
nitric acid was added, and the mixture evaporated (without boiling)
to a final volume of 3 ml. The residue was taken up in 5 ml. of
water, and a complete reagent blank was carried through an identi-
cal treatment. Cobalt was determined by the standard thiocyanate
acetone method (31), and nickel by dimethyldioxime (31). The
Beer's law calibration curves used in these colorimetric methods
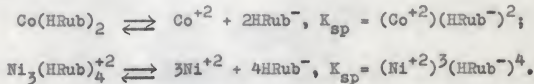are shown in Plate III.

The molar solubility values obtained experimentally were
5.50 ($\pm$ 0.21) $\times 10^{-5}$ for cobalt rubeanate and 7.50 ($\pm$ 0.25) x

10^{-7} for nickel rubeanate. For the three rubeanates studies, the order of decreasing solubility is Co > Ni > Cu, which is the same order as the increasing stabilities of complexes formed by these metals with ligands such as ethylenediamine. In contrast the sequence for decreasing solubilities of the sulfides is Ni > Co > Cu.

Portions of solid cobalt and nickel rubeanates were isolated for elemental analysis. These materials were obtained by precipitation from dilute solutions (0.001 molar) of the metal ions and dithiooxamide that were buffered at pH 7. Under these conditions the likelihood of coprecipitation of dithiooxamide is minimized and a slow rate of precipitation is achieved. The precipitates were allowed to stand for three days prior to filtering, and, after washing the precipitates thoroughly with water, the final washings were made with ethanol. These metal rubeanates were dried at room temperature in a manner like that used for copper rubeanate. As a preliminary treatment of samples for analysis for the metal content, accurately weighed portions were decomposed with nitric acid. Since the amounts of isolated solids were small, analytical samples were limited to the thirty to fifty milligram range. This necessitated the use of gravimetric determinations of the metals by reagents of suitable gravimetric factor rather than by electrodeposition methods. Nickel was determined by the standard dimethyldioxime procedure (16), and cobalt was precipitated as potassium cobaltinitrite but was finally weighed as the anhydrous sulfate (16). From duplicate determinations,

the mole ratio of nickel to rubeanate was found to be 3 to 4, and that for cobalt to rubeanate was 1 to 2. (Duplicates were reproducible within two percent). These ratios differ from those reported in other investigations (28, 29, 38), but the latter have been determined on products obtained under different (and in some cases less stringent) conditions for precipitation than were employed here.

Although it appears probable that the metal rubeanates are polymeric, the values for the molar solubilities can be used with the above empirical formulae to calculate approximate solubility product constants. The appropriate equilibrium expressions are:

$$Co(HRub)_2 \rightleftharpoons Co^{+2} + 2HRub^-, \; K_{sp} = (Co^{+2})(HRub^-)^2;$$
$$Ni_3(HRub)_4^{+2} \rightleftharpoons 3Ni^{+2} + 4HRub^-, \; K_{sp} = (Ni^{+2})^3(HRub^-)^4.$$

The K_{sp} values calculated upon the basis of these equations are $6.65 \; (\pm 0.26) \times 10^{-13}$ for cobalt rubeanate and $1.34 \; (\pm 0.40) \times 10^{-43}$ for nickel rubeanate, at ionic strength of 0.02 and pH 7.00 in both cases.

Structures for the Rubeanates

The structure of rubeanic acid and the rubeanate ion govern to a major extent the structures of the metal rubeanates. Although it has been demonstrated that the predominate ionic species in solutions of dithiooxamide is the ion formed by the removal of

hydrogen ion from the amidoimido form, the structure of this ion needs to be more closely examined as a chelating agent.

If the weakly acidic ionization is ignored, the dithiooxamide molecule can be written in two forms,

$$
\begin{array}{ccc}
H_2N & & NH_2 \\
\quad\diagdown & & \diagup \\
C = S & \quad\text{and}\quad & S = C \\
\mid & & \mid \\
C = S & & C = S \\
\diagup & & \diagdown \\
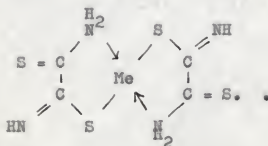H_2N & & H_2N \\
\end{array}
$$

corresponding to cis and trans forms with respect to the orientation of the sulfur or nitrogen atoms. The single-bonded carbons allow unhindered free rotation; however, the presence of the two pairs of dissimilar nonmetallic atoms in the molecule makes it unlikely that both the cis and trans forms are present in equal amounts. The covalent radius of 1.04 A. for sulfur, as compared to the 0.77 A. value for carbon, as well as the strong orbital overlap for the doubly-bonded sulfur, make it probable that the trans form is the preferred orientation. (A similar, though not completely analogous, example of this type of preferred trans configuration is the well known case of 1,2-dibromoethane). The cis form might conceivably be stabilized through hydrogen bonding by one of the monothiol forms and the remaining sulfide sulfur, but hydrogen bonding does not occur to an great extent with second period elements. Likewise, hydrogen sulfide itself does not show hydrogen bonding. Therefore, it is most probable that the chelating species in solutions of dithiooxamide is the ion derived from

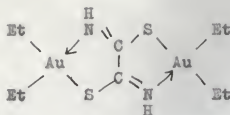the monoacidic dissociation of the trans form, and having the
structure

$$-S-C \overset{\displaystyle NH}{\underset{\displaystyle \underset{H_2N}{C=S}}{\|}}\quad .$$
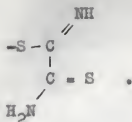
The general structural formula proposed by Ray (23, 29) and
Feigl (12) in which the metal is bonded through two five-membered
rings to a divalent rubeanate ion has two weaknesses: (1) all
divalent metallic ions should yield products in which the ratio
of metal to rubeanate is 1 to 1: and (2) the metallic ion can
show a coordination number of four only. Likewise, scale mole-
cular models show that such a structure would require a very
strained rubeanate structure bonded to the metal through bond
distances of three to four times the normal distances for che-
lation. The empirical formula determinations reported by Tana-
naev (38) and Bobtelsky (7), as well as those found in this
study, indicate that no single structural formula is applicable
to all metal rubeanates. The structure proposed above for the
rubeanate ion indicates that the metal could form five-membered
rings of the type

$$S=C \overset{\displaystyle \overset{H_2N}{\big\downarrow}}{\underset{\displaystyle \underset{HN}{\overset{\|}{C}}}{}} \quad Me \quad \overset{\displaystyle S}{\underset{\displaystyle \underset{N_2}{\overset{\|}{C}}}{}} \overset{\displaystyle NH}{\underset{\displaystyle C=S}{\|}} \quad .$$

Such a molecule can be constructed easily from scale models for metals showing both square-planar and tetrahedral directional coordination, and yielding planar structures like that above or those with one of the rings approximately perpendicular to the plane of the paper. However, in those cases where the metal shows only a coordination number of one, as in the rubeanates of copper, ruthenium, gold, and palladium, ring formation may not necessarily be involved. Infrared studies on thiourea complexes showed that sulfur-to-metal bonds are formed for the group eight metals in contrast to nitrogen-to-metal bonds found in urea complexes (48). It is evident that all of the coordination sights on the one to one metal rubeanates are not satisfied, for these can be dissolved to varying degree in such coordinating solvents as acetone, dioxane, and pyridine, but are not dissolved by ionic nor non-polar solvents. Only in acidic media are such one to one rubeanates formed, and water soluble species are obtained with ruthenium (47) and some of the platinum group metals. The slight solubility of the rubeanates of palladium, ruthenium, cobalt, and copper, in polar organic solvents suggests that compounds of definite structure like that represented above may exist as molecular species. Evidence supporting this type of structure has been presented by Ewens and Gibson (11) from an analysis of the reaction between diethylgold and rubeanic acid. On the basis of molecular weight determinations, solubility behavior, and derivatives prepared, the structure

$$
\begin{array}{c}
\text{Et} \quad\quad \overset{\text{H}}{\text{N}} \nwarrow \text{C} - \text{S} \quad\quad \text{Et} \\
 \searrow \;\; \text{Au} \swarrow \quad\quad \searrow \text{Au} \nearrow \\
\text{Et} \quad\quad \text{S} \nearrow \text{C} = \underset{\text{H}}{\text{N}} \quad\quad \text{Et}
\end{array}
$$

was assigned. While differing in the identification of the reactive species of rubeanic acid, the results of Ewens and Gibson do verify the bridge structure involving two five-membered rings. Such S-CC-N rings have been assigned to the structures of cobalt-cysteine chelates, which also show extreme insolubility (22).

Rubeanates precipitated from alkaline and neutral media have mole ratios of rubeanate to metal greater than one, as in Ni_3R_4, $Pd_2R_3(7)$, and $Au_2R_3(7)$. Such products are generally insoluble in all types of solvents, from the very polar to the non-polar, and precipitate slowly from solution. Also, they show surprising resistance to attack by mineral acids at the 6M. level. The general inertness of these rubeanates suggests that they are polymeric substances, and the higher the formula weight the more closely the mole ratio approaches the limiting value of one to one. Jensen (18) first suggested a chain polymeric structure of four-membered rings for alternating metal and rubeanate groups. Also, five-membered ring structures of alternating groups have been proposed (11). However, either structure for the chains would account for the diamagnetism observed for nickel rubeanate (18). Since empirical formulae determined for such polymeric mixtures correspond only to the "average molecule", calculated solubility products are not meaningful in their strictly literal sense.

The formation of such 1:1 polymers does not necessarily require initial reaction between the metal ion and a divalent rubeanate anion. It is possible that the terminal rubeanate group of a growing chain polymer may undergo ionization and coordinate with another metal ion, and continue the growth. This is consistent with the slow rate of precipitation.

SUMMARY

In aqueous solutions the weakly acidic behavior of dithiooxamide (rubeanic acid) is attributable primarily to the monobasic acid ionization of this compound. From potentiometric titrations, K_a, K_{sp}, and the molar solubility, S_A, were evaluated at various ionic strengths: $K_{a_1} = 6.54$ to 6.80×10^{-11}; $K_{sp} = 2.25$ to 2.84×10^{-13}; and $S_A = 3.88$ to 4.17×10^{-3} moles per liter for ionic strength from 0.01 to 1.0. A direct spectrophotometric determination of S_A gave 4.04 to 4.84×10^{-3} moles per liter for solutions having ionic strengths in the same range. Graphic representation of solubility as a function of ionic strength demonstrated that dithiooxamide conforms to the Debye-Huckel prediction for the behavior of a 1:1 weak electrolyte.

From changes in the near ultraviolet absorption spectrum of dimethylformamide solutions of dithiooxamide exhibited in the presence of base, the identities of various molecular and ionic species in solution were determined. The evidence indicated that most of the compound exists as the diamido form, and that the amido-imido form is the predominant ionic species in basic
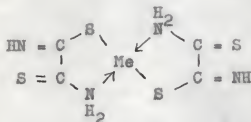
solutions. Although the diimido form probably exists in strongly
alkaline media, no quantitative information on its ionization
could be obtained. In dimethylformamide the first acid dissocia-
tion constant of dithiooxamide was found to have a value of 4.1 x
10^{-4}. Two tautomeric equilibrium constants were also computed:
$K_{T_1} = 0.74$; and $K_{T_3} = 0.0204$.

The qualitative solubility of the rubeanates of copper,
cobalt, and nickel, in various organic solvents was investigated.
In general these compounds showed no appreciable solubility in
water miscible or water immiscible solvents. Only slight solubil-
ity was observed for the cobalt and copper rubeanates in such
coordinating solvents as acetone and dioxane, suggesting that all
of the coordination positions on the metals may not be involved
in bonding to the rubeanate ion.

The solubilities of the rubeanates of copper, cobalt, and
nickel were determined quantitatively in buffered aqueous solu-
tions at ionic strength of 0.02. In terms of the concentration
of soluble metallic ion, the molar solubilities of the rubeanates
were found to be: 3.90×10^{-7} for copper at pH 4.6; 5.50×10^{-5}
for cobalt at pH 7.0; and 7.50×10^{-7} for nickel at pH 7.0. Pre-
cipitates isolated from dilute solutions were analyzed for their
metal content, and empirical formulae were assigned. If the
rubeanate portion of the molecule is designated by R, the form-
ulae obtained were CuR . acetate, CoR_2, and Ni_3R_4. Solubility
product constants were computed upon the basis of these formulae,
but in view of the possible polymeric nature of these insoluble

rubeanates the constants have little meaning.

In terms of probable structures, the metal rubeanates may
be placed in two groups. The first group includes those obtained
from acid media, possessing significant water solubility and/or
solubility in coordinating organic solvents, and these have been
given discrete molecular structures. Such formulae involve the
coordination of the metal ion with one or two rubeanate ions by
five-membered ring formation of the type given below.

$$HN = C \overset{S}{\underset{\underset{\displaystyle N}{|} H_2}{\diagdown}} \quad \overset{H_2}{\overset{N}{\diagdown}} \quad C = S$$

$$S = C \diagup \quad Me \quad \diagdown \quad C = NH$$

The second group of metal rubeanates are those formed in alkaline
media and possess properties of polymers. The structures of these
are generally pictured as chains composed of alternating rubeanate
ions linked together through coordination with metal ions.

ACKNOWLEDGMENT

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DITHIOOXAMIDE AS AN ANALYTICAL REAGENT

by

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B. A., Friends University, 1948
M. A., Washington University, 1950

AN ABSTRACT OF A THESIS

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1958

Dithiooxamide (also called rubeanic acid) is a very sensitive reagent for the detection of trace amounts of copper, cobalt, nickel, and some of the platinum group metals. It was the purpose of this study to attempt to identify the reactive species of dithiooxamide in solution, to obtain quantitative data on the solubilities of the rubeanates of copper, cobalt, and nickel, and to propose suitable structures for the rubeanates.

From potentiometric titrations in aqueous and non-aqueous solutions, it was demonstrated that the weakly acidic behavior of dithiooxamide is due primarily to the monobasic ionization of this compound. The acid dissociation constant, solubility product, and molar solubility for aqueous solutions are 6.5×10^{-11}, 2.2×10^{-13}, and 3.9×10^{-3}, respectively. The change in solubility with ionic strength conforms to the Debye-Huckel prediction for a 1:1 weak electrolyte.

The examination of the absorption spectra of dithiooxamide in methanol and dimethylformamide as solvents, and the changes in the spectra produced by base, permitted the identification of several species of the solute existing in solution. Most of the compound exists in the diamido form, and the predominant ionic species is the amido-imido form. Although the diimido form may exist in strongly alkaline media, no quantitative information on its ionization could be obtained. In dimethylformamide the first ionization constant of dithiooxamide is 10^{7} times greater than in water solution.

The rubeanates of copper, cobalt, and nickel show no appreci-

able solubility in water miscible or immiscible solvents. The slight solubility of the cobalt and copper rubeanates in such coordinating solvents as acetone and dioxane suggests that not all of the coordination positions in the metals are bonded to the rubeanate ion. Analysis of solid rubeanates for their metal content indicated that the ratio of metal to rubeanate is 1:1 for copper, 1:2 for cobalt, and 3:4 for nickel. The order of decreasing molar solubility for the three rubeanates studied is Co > Ni > Cu.

For rubeanates possessing simple molecular formulae, it is probable that the metal reacts with one or two rubeanate ions in the trans amido-imido form to produce five-membered ring chelate structures. The evidence supports the view that polymeric chain structures are present in more complex rubeanates, as exemplified by that of nickel. Consequently, no single structure adequately represents all rubeanates.