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Nature and Cumulative Stability Constants of Copper(I) Complexes of Some Substituted Thioureas

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The cumulative stability constants of the bis, tris, and tetrakis complexes of thiourea and 14 substituted thioureas with copper(I) are computed from dc polarographic data. Mono complexes are believed to have little significance in these equilibria. The very high stability of these complexes, even in strongly acidic media, is explained in terms of their molecular orbital configurations.

Introduction

In the acidic dissolution of encrustations containing copper and iron oxides from power plant boilers it is common practice to incorporate a copper complexing agent in the acid to facilitate the removal of copper in a soluble form.[1-3] For this application the copper(I) complexes of lower thiourea homologues present an interesting and unique case, because in such complexes copper(I) is appreciably soluble in strongly acidic solutions and is highly stable toward disproportionation.

The literature abounds with examples of soluble, stable complex ions formed between copper(I) and ligands containing a basic amine functionality. However, the mode of complexation in these examples is such that the complex ions lose all identity in acidic media. Further, there are many ligands which form stable complexes with copper(I) in neutral and acidic media, but these have low aqueous solubility, for example, the dithiocarbamates used in solvent extraction of metal ions from acidic aqueous media.[4] The halide complexes of copper(I) represent a class which might challenge the singularity of the thiourea homologues; however, the relatively low stabilities of these complexes make them unusable in the above application. That application requires that copper be prevented from redeposition (as metallic copper) on ferrous metal surfaces.

In the presence of excess ligand, copper(I) is soluble to an extent of several grams per liter as a complex of these thiourea homologues. In addition these complexes are highly stable in acid—sufficiently stable, in fact, that there is no plating of copper from such a complexed copper solution onto ferrous metal walls.[5] This appreciable solubility and the high stability are the properties that prompted the present interest in these complexes.

The stability constants of the copper(I) complexes of some thiourea homologues have been reported in the literature. Lane, Quagliano, and Bertin[6] reported the polarographically determined stability constants of tetrakis complexes with thiourea and imidazolidine-2-thione to be 4.2×10^{15} and 1.7×10^{15}, respectively. The former value is in fair agreement with the results of Onstatt and Laitinen,[7] who found the stability constant for the tetrakis(thiourea)–copper(I) complex to be 2.4×10^{15}. A different value, 6.7×10^{12}, was reported by Pilipenko,[8] who determined the stability constant by a potentiometric method. In a later publication Lane[9] compared the stabilities of the copper(I) complexes of some methyl- and ethyl-substituted thioureas.

We note that these previous investigations all limited their attention to the tetrakis complexes. In the present report, the stability constants of bis and tris complexes, as well as those of tetrakis complexes, of several thiourea homologues are calculated from polarographic data. Also, we present a discussion of the mode of complexation, considered from a molecular orbital standpoint.

Experimental Section

Materials. Imidazolidine-2-thione, 4-methylimidazolidine-2-thione, 4,4-dimethylimidazolidine-2-thione, and hexahydropyrimidine-2-thione were prepared by allowing CS_2 to react with the respective diamines.[10] The method of Hurwitz and Auten[11] was used for the preparation of 1-(2-aminoethyl)imidazolidine-2-thione. The remaining ligand compounds were obtained from Roberts Chemicals Co., Nitro, W.Va. All of these compounds were further purified by recrystallization.

The most acceptable way for introducing copper(I) into the electrolysis solutions was as the complex of the particular ligand under investigation. Each copper(I) complex was prepared in an acidic aqueous medium by the addition of CuCl (1–3%) to an approximately 3% solution of ligand. Solvent was slowly evaporated until precipitation occurred. The precipitated complex was then recrystallized from a water solution of the ligand.

Apparatus. Current–voltage curves were obtained with a Sargent Model XVI recording polarograph. Accurate measurements of half-wave potentials were made through calibration of the "%-span emf applied" with an Orion Model 801 potentiometer. A polarographic H cell with an agar–KCl salt bridge was used as the electrolysis cell. Potential measurements were made vs. a saturated calomel electrode. The capillary constant, determined in 0.1 N HCl at 25 ± 0.2 °C and at an applied potential of −0.6 V, had a value 1.42 $mg^{2/3}\ s^{1/6}$ for a mercury column height of 47 cm.

Sample Preparation. In preparing solutions for analysis, varying weights of ligand were used along with sufficient weight of the copper complex to yield solutions 10^{-3} M in copper. HCl, 0.1 N, was used as the supporting electrolyte, and 0.01% Triton X-100 was used as a maximum suppressor. Tank nitrogen, passed through a heated copper gauze for oxygen removal, was used for deaeration of samples before electrolysis.

In the case of 1-(2-aminoethyl)imidazolidine-2-thione enough HCl was made to neutralize the amine and still maintain a final HCl concentration of 0.1 N. To maintain constant ionic strength among individual samples of this series, appropriate amounts of KCl were added to each sample. Total chloride ion concentration in the 1-(2-aminoethyl)imidazolidine-2-thione series was 0.514 N.

Results

The polarographic method for determination of stability constants of metal complexes relates the equilibrium concentration of the free metal ion to half-wave potentials ($E_{1/2}$). In the simplest cases in which only one complex species exists in solution, the classic graphical method outlined by Kolthoff and Lingane[12] can be conveniently used. By measuring $E_{1/2}$ values for solutions of the metal ion containing varying concentrations of ligand, one can determine both the coordination number of the central ion and the cumulative stability constant of the complex using the equation

$$(E_{1/2})_s - (E_{1/2})_c = \frac{0.0592}{n} \log \beta_p + p\frac{0.0592}{n} \log C_L \qquad (1)$$

where $(E_{1/2})_c$ is the measured half-wave potential and $(E_{1/2})_s$ is the half-wave potential for reduction of the simple copper(I) ion. The term C_L represents the molar concentration of ligand, and β_p is the cumulative stability constant to be measured. The

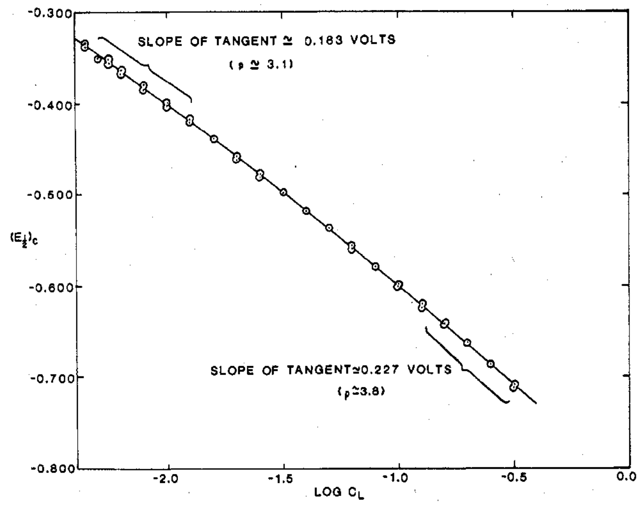

Figure 1. Polarographic data for 0.00438–0.361 M hexahydropyrimidine-2-thione with 0.001 M Cu(I).

Table I. Elemental Analysis of Precipitates from Copper(I) Solutions Containing Dilute Ligand

	%C	%H	%N
Precipitate from thiourea	7.0	2.4	15.5
Calcd for $Cu(CH_4N_2S)Cl$	6.9	2.3	16.0
Precipitate from hexahydropyrimidine-2-thione	21.4	3.9	12.5
Calcd for $Cu(C_4H_8N_2S)Cl$	22.0	3.7	13.0

terms p and n represent the coordination number of the central copper(I) ion and the number of electrons involved in the reduction of a copper(I) ion, respectively. The validity of this equation is, necessarily, predicated on the true reversibility of the chemical equilibrium (eq 2) and the electrode reaction (eq

$$Cu(lig)_p{}^+ \rightleftarrows Cu^+ + p(lig) \qquad (2)$$

3). Plots of log $[(i_d - i)/i]$ vs. E were made for the copper

$$Cu^+ + e^- \rightleftarrows Cu^0 \qquad (3)$$

complexes of all 15 thiourea homologues and in all cases the slopes indicated reversible one-electron reductions.

All reported polarographic determinations of the stability constants of copper complexes of thiourea and its homologues have been based on the assumption that only tetrakis complexes are formed.[6,7,9] Indeed, at the high ligand-to-copper concentration ratios examined in those reports, such an assumption may have been justified. The plots of $(E_{1/2})_c$ vs. log C_L appeared to be straight-line functions with slopes indicating $p = 4$. However, when one examines a wider range of ligand concentrations, the deviation from linearity becomes apparent, as is seen in Figure 1. In the region of the curve representative of data taken from solutions of high ligand concentration, a tangent to the curve has a slope very near the value 0.237 V/decade indicative of a predominantly tetrakis complex; however, at lower ligand concentrations a tangent drawn to the curve has a substantially lower slope, thus suggesting the presence of lower coordinated complexes. This is demonstrated in Figure 1 for a specific example (the ligand hexahydropyrimidine-2-thione), and it has been observed in all 15 of the ligands investigated.

The presence of lower coordinated complexes was confirmed in this work by an independent qualitative observation. Namely, in all solutions prepared to contain only an approximately 5:1 molar excess or less of ligand to copper(I), precipitates resulted. This was a general observation for all ligands of this class. Elemental analyses of two specific examples of these precipitates showed them to be the mono complexes, as is seen in Table I.

These observations pointed to the necessity of treating the data by a method capable of evaluating successive stability constants. Basically, eq 4, derived by DeFord and Hume,[13]

$$\sum_p \beta_p (C_L)^p = \text{antilog}\ \frac{(E_{1/2})_s - (E_{1/2})_c}{0.0592} \qquad (4)$$

was used after certain simplifying assumptions. The ratio of the activity coefficients of the simple and complex ions and the ratio of the diffusion current constants of simple and complex ions are assumed to be unity. This, of course, means that the calculated constants in this report are "concentration constants" and not truly thermodynamic values.

A further assumption made in these calculations was the absence of polynuclear, or cluster, complex species in solution. Polynuclear species have been shown to exist with thiourea and metal ions,[20] at least in the crystalline state; however, their existence under conditions of dilute aqueous solution has not been seriously considered in the literature. For example, Lane's[9] treatment of thiourea complexes of lead and cadmium considers no polynuclear contribution.

A further examination of the slopes of the sample curve in Figure 1 indicates the predominant complex species to be the tris and tetrakis complexes. Neither in this sample curve nor in similar curves plotted for the other ligands under investigation was there any suggestion of a significant contribution due to mono complexes. In fact, based on the elemental analyses in Table I, it may be concluded that no significant concentration of the mono complex can exist in solution due to low solubility of the mono complex. Thus, even under conditions where it might be favored, the mono complex precipitates from solution, leaving only the higher complexes in solution in significant concentration.

After the above considerations, the final form of the equation used in these calculations was

$$\beta_2 C_L{}^2 + \beta_3 C_L{}^3 + \beta_4 C_L{}^4 = \text{antilog}\ \frac{0.143 - (E_{1/2})_c}{0.0592} \qquad (5)$$

where the value of $(E_{1/2})_s$ for copper(I), not directly measurable, was taken to be +0.143 V.[7] Values for β_2, β_3, and β_4 were calculated by a computer solution of simultaneous linear equations. In the execution of the program, all possible combinations were solved except those which yielded nonpositive values. The data set was further reduced by imposing a 3σ limitation. The results of these calculations are shown in Table II with error expressed as percent standard deviation.

The present mathematical problem determines chemical equilibrium constants from a set of equations, nonlinear in the variable $(E_{1/2})_c$, but with transformations on this variable to generate a set of linear equations. This, unfortunately, leads to a very sensitive dependence of β_2, β_3, and β_4 (eq 5) on the experimentally measured parameter $(E_{1/2})_c$. It is beyond the scope and intent of the present report to deal with this generally acknowledged limitation in the mathematical model, but it does make these and all such calculations subject to relatively large error. Within this context, we feel that the standard deviations for the determinations reported in Table II are generally quite good. Exceptions will be specifically discussed.

There are three ligands for which the β_4 determinations have noticeably higher error than for others: 1-(2-hydroxyethyl)imidazolidine-2-thione, 1,3-diallythiourea, and 1,3-diethylthiourea. In all three cases, and in only these three, low ligand solubility placed a serious upper limit on concentrations analyzed (C_L). Thus, in these three cases, solutions of high ligand concentration were not accessible to experiment. Since it is specifically at high ligand concentrations where the tetrakis complex would predominate (see Figure 1), data points most sensitively affected by the tetrakis complexes are absent.

The relative errors in the β_3 determinations are consistently somewhat larger than those of the respective β_4 determinations. In all probability, this reduced reliability for the β_3 deter-

Table II. Cumulative Stability Constants and Standard Deviations

Name	β_2	σ, %	β_3	σ, %	β_4	σ, %
Hexahydropyrimidine-2-thione	6.1×10^{12}	140	9.6×10^{14}	36	2.7×10^{16}	27
4-Methylimidazolidine-2-thione	2.7×10^{12}	76	6.0×10^{13}	33	1.3×10^{15}	18
4,4-Dimethylimidazolidine-2-thione	1.1×10^{12}	57	4.5×10^{13}	42	1.5×10^{15}	12
1-(2-Aminoethyl)imidazolidine-2-thione (HCl)	1.9×10^{10}	47	4.6×10^{11}	36	7.3×10^{12}	26
1-(2-Hydroxyethyl)imidazolidine-2-thione	2.2×10^{11}	40	1.0×10^{13}	23	1.2×10^{14}	48
Imidazolidine-2-thione	8.1×10^{11}	64	3.3×10^{13}	38	7.3×10^{14}	19
Tetrahydro-3,5-dimethyl-4*H*-1,3,5-oxadiazine-4-thione	2.1×10^{11}	50	7.4×10^{12}	59	1.4×10^{14}	27
Thiourea	2.0×10^{12}	71	2.0×10^{14}	34	3.4×10^{15}	18
1-Acetylthiourea	3.4×10^{11}	51	5.6×10^{12}	43	6.5×10^{13}	29
1-Allylthiourea	1.5×10^{13}	71	3.8×10^{14}	40	7.9×10^{15}	12
1,3-Diallylthiourea	1.0×10^{13}	25	2.7×10^{14}	35	3.8×10^{15}	64
1-Methylthiourea	1.9×10^{13}	88	2.9×10^{14}	35	3.3×10^{15}	11
1,3-Dimethylthiourea	3.3×10^{12}	65	8.2×10^{13}	28	9.6×10^{14}	18
1-Ethylthiourea	1.2×10^{13}	74	2.6×10^{14}	40	1.7×10^{16}	3
1,3-Diethylthiourea	1.1×10^{14}	33	1.0×10^{15}	49	7.4×10^{15}	75

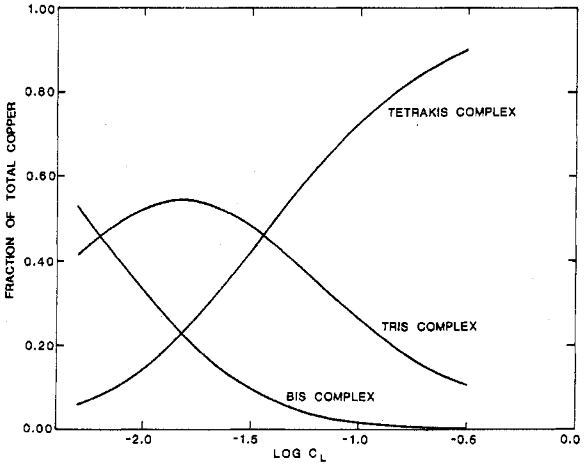

Figure 2. Distribution of copper(I) among the various hexahydropyrimidine-2-thione complexes as a function of hexahydropyrimidine-2-thione concentration.

mination reflects a lower equilibrium concentration of tris complexes, relative to the tetrakis complexes, over most of the accessible ligand concentration range. The relative errors in the β_2 determinations are, likewise, generally larger than those for either the β_3 or β_4 determinations. Again, this probably suggests a lesser significance of the bis complexes in the equilibrium in the concentration range investigated. Plots of the distribution of copper(I) between the various complexes as a function of ligand concentration bear this out. A sample curve for hexahydropyrimidine-2-thione is shown in Figure 2.

Discussion

The high stability in an acid medium (pH 1) of the thiourea complexor when compared to ordinary Lewis base–metal complexor is remarkable. For example, when an amine–copper complex is placed in an acidic environment, the complex immediately uncouples due to the equilibrium

$$M^{n+}D_m + mH^+ \rightleftarrows M^{n+} + mDH^+$$

where D is the Lewis base donor. This fact leads one to hypothesize that a different bonding mechanism is occurring between the copper(I) and thiourea-type ligands.

One way in which such a mechanism could be formulated is through a synergistic effect operating between the metal atom and the ligand. The mechanism is formulated completely analogously to that accepted as occurring in the case of metal–carbonyl complexes. First there is a dative overlap of a filled ligand orbital with an empty metal orbital to form a σ bond. The metal in turn donates electrons to an empty ligand orbital. The mechanism is synergic, insofar as electron density is back-donated to the ligand from the metal, the metal center becomes more positive, and the ligand becomes more basic, thereby providing an even greater driving force for the formation of a stronger primary σ bond. When such a mechanism is operative, it can be especially utilitarian in acidic solution, because the presence of hydrogen ion does not interfere in the formation of the complex species, as is the case when amines are present. This is, of course, due to the extra driving force favoring the formation of the metal–thiourea complex.

This type of bonding for copper(I) with olefin linkages has been amply described in a recent article by Salomon and Kochi.[15] More relevant to this article are the discussions given by Spofford and Amma[16,17] and by Hanic and Durcauska.[18] The crystal structures described by these authors for the bis(thiourea)copper(I) chloride and tris(thiourea)copper(I) perchlorate, respectively, demonstrate that such a mechanism is possible. In these papers, two types of bonding were observed. One mode of bonding was postulated as occurring via a donation of electrons from the pπ S–C molecular orbital of thiourea to a hybrid set of orbitals on the copper atom (sp^2 in the case of the bis complex, sp^3 in the case of the tris complex). Back-donation from the metal to the ligand orbital is suggested as occurring from the filled "d^{10}" configuration of the copper(I) ion either to a low-energy empty "d" orbital of sulfur or to the "a_1" antibonding π^* molecular orbital. The other mode of thiourea to copper bonding occurs via donation of nonbonding S electrons to the copper atom. This latter form of bonding does not preclude a synergistic mechanism being operative here also. Succinctly stated, thiourea-type ligands have a high affinity for polarizable Lewis acids capable of back-bonding relative to nonpolarizable Lewis acids not capable of back-bonding.

Assuming that a synergistic mode of bonding is the mechanism that explains the stability of the complexes in acidic solution, one is tempted to draw further conclusions about the nature of the bonding, based upon certain qualitative experiments. Sulfur-containing ligands such as 2-mercaptoethanol and β-mercaptopropionic acid readily form complexes with copper(I) in acidic solution. Since neither of these ligands has the extensive π molecular orbital available for back-donation, the suggestion of Spofford and Amma[17] that the back-donation is to empty "d" orbitals on the sulfur atom is reinforced.

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Registry No. Cu(hexahydropyrimidine-2-thione)$_4^+$, 52880-74-7; Cu(4-methylimidazolidine-2-thione)$_4^+$, 58188-35-5; Cu(4,4-dimethylimidazolidine-2-thione)$_4^+$, 58188-36-6; Cu(1-(2-aminoethyl)imidazolidine-2-thione)$_4^+$, 58188-37-7; Cu(1-(2-hydroxyethyl)imidazolidine-2-thione)$_4^+$, 58188-38-8; Cu(imidazolidine-2-

thione)$_4{}^+$, 47421-11-4; Cu(tetrahydro-3,5-dimethyl-4*H*-1,3,5-oxadiazene-4-thione), 58188-39-9; Cu(thiourea)$_4{}^+$, 36252-51-4; Cu(1-acetylthiourea)$_4{}^+$, 58188-40-2; Cu(1-allylthiourea)$_4{}^+$, 58188-41-3; Cu(1,3-diallylthiourea)$_4{}^+$, 58188-42-4; Cu(1-methylthiourea)$_4{}^+$, 58188-43-5; Cu(1,3-dimethylthiourea)$_4{}^+$, 31248-33-6; Cu(1-ethylthiourea)$_4{}^+$, 58188-44-6; Cu(1,3-diethylthiourea)$_4{}^+$, 58188-45-7.

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Metal Complexes of Free Radicals. IV.[1] Electrolytic Generation, Complex Equilibria, and Electronic Structure

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The radical–ligand complex Zn(glir)$^+$, where glir$^-$ is the radical anion of glyoxal bis(*N-tert*-butylimine), has been generated by an electrolytic method within the ESR cavity. This species shows further complex formation with other ligands X. In the case of unidentate ligands X (X$^-$ = Cl$^-$, Br$^-$, I$^-$, NCS$^-$, NCO$^-$, N$_3{}^-$) 1:1 and 1:2 complexes (only 1:1 for I$^-$) are formed in a stepwise manner. With the bidentate ligand en only a 1:1 complex was observed. A complex with two coordinated diimine ligands which are in a collectively reduced ground state has also been observed. SCCC–MO calculations are in qualitative agreement with the observed ESR parameters.

Introduction

In the previously applied methods[2] for the preparation of radical complexes of the type M(diir)X$_n$, where diir is the radical anion[3] of an α-diimine ligand, an alkali metal M′ or the metal M forming the complex was used as the reducing agent. The former is a two-step and the latter a one-step reaction as shown for an example by eq 1 and 2, where gli = glyoxal bis(*N-tert*-butylimine) and glir$^-$ = radical anion of gli.

$$\mathrm{K + gli \rightarrow K^+ + glir^-} \tag{1a}$$

$$\mathrm{ZnX_2 + glir^- \rightarrow Zn(glir)X}_n + (2 - n)\mathrm{X}^- \quad (n = 1 \text{ or } 2) \tag{1b}$$

$$\mathrm{Zn + ZnX_2 + 2gli \rightarrow 2Zn(glir)X} \tag{2}$$

Because of the extreme sensitivity of the radical complexes the preparations are carried out[2] in an all-glass system sealed after complete degassing on a vacuum line. This method is therefore not suitable for the investigation of concentration-dependent phenomena, because it does not allow a precisely controlled variation of the concentrations.

An electrolytic cell (see Experimental Section) was developed in which radical complexes can be produced in the ESR cavity and which allows at the same time for a controlled change of concentrations of the reactants. The concentration-dependent studies were conducted with the aim of establishing the nature of equilibria involving complexes M(glir)X$_n$ by varying n and using different ligands X. The spin-labeled ligand[4] glir$^-$ serves as a convenient probe for detection of these complexes and also for the spin density distribution, since the magnetic nuclei in the coordinated glir *and* in the ligands X give rise to hyperfine splittings. This provides some of the most direct information available on electron delocalization in complexes of d^{10} or d^0 metal ions and will be correlated with results from semiempirical calculations. Another advantage of the electrolytic method is the possibility of carrying out reductions in solvents with a high dielectric constant, such as dimethylformamide (DMF), with a consequently much higher solubility of the metal compounds compared with the dimethoxyethane (DME) or tetrahydrofuran (THF), which were used for alkali metal reduction.

Experimental Section[1b]

A. Materials. All chemicals, unless indicated below, were of the highest purity obtainable and were used as received.

Dimethylformamide (Fluka puriss), which was used as a general solvent for all the experiments described in this paper, was shaken for 2 h with NaOH pellets and then for 2 h with KH$_2$PO$_4$ (dried at 140 °C), filtered, distilled at 80 °C over molecular sieves (Union Carbide 3 Å), and stored in an argon atmosphere over molecular sieves. Before use it was distilled directly from the storage vessel into a container connected to the electrolytic cell.

Argon was purified with BTS-Catalyst (Fluka AG) and then dried over P$_2$O$_5$.

Zn(DMF)$_6$(ClO$_4$)$_2$ was prepared according to a reported method[5] and analyzed for Zn.

Glyoxal bis(*N-tert*-butylimine) was prepared as described before.[2]

Tetraethylammonium perchlorate (TEAP) was obtained from a solution of tetraethylammonium hydroxide (Fluka) and perchloric acid. It was recrystallized two or three times until it showed no impurity in a polarogram in DMF (10^{-1} M solution).

The anionic ligands Cl$^-$, Br$^-$, I$^-$, NCS$^-$, and NCO$^-$, were all introduced in the solution as their tetraethylammonium salts. These were prepared either by neutralization of the hydroxide with the corresponding acids (Cl$^-$, Br$^-$, I$^-$, NCS$^-$) or by metathetical reactions (exchange of Br$^-$ with AgNCO). Azide ion was introduced as sodium azide.

Ethylenediamine was stored over NaOH and was freshly distilled before use.