$$1/\overline{P}_n = C_{tr,m} + C_{tr,s}\frac{[S]}{[M]} + C_{tr,cat}\frac{[Cat]}{[M]} + \frac{A'R_p}{[M]^2} \quad (5)$$

In the above equation, $C_{tr,m}$ is the chain transfer constant to the monomer, $C_{tr,Cat}$ is the chain transfer constant to the catalyst, and $C_{tr,S}$ is the chain transfer constant to any other substance in the system, in this case the activator dimethylaniline.

The results outlined in equation 4 are in reasonably good agreement with those obtained using 2-azobisisobutyronitrile as the catalyst.[1] Since both activator concentration [S] and catalyst concentration [Cat] are non-linear functions of $R_p$, one would not get the relation given in equation 4 unless the terms $C_{tr,s}$ [S]/[M] and $C_{tr,cat}$ [Cat]/[M] were negligible under the experimental conditions studied.

The fact that small quantities of dimethylaniline did not affect the $R_p$ or $\overline{P}_n$ of a 2-azobisisobutyronitrile initiated polymerization shows that dimethylaniline does not affect the termination or propagation steps of the chain reaction.

The role of dimethylaniline in the $Bz_2O_2$–DMA initiated systems must therefore be entirely in the initiation step.

The kinetic result for $R_p$ at 0° (see equation 3a) is readily understood. The rate of initiation $R_i'$ is related to the rate of polymerization $R_p$ by means of the equation

$$R_i' = \frac{2A'}{[M]^2}R_p^2 \quad (6)$$

Moreover $A'$ is defined in equation 5. $A'/[M]^2$ at 0° is determined by the slope of the straight line defined in equation 4a, namely, 640. Substituting this value and the value of $R_p$ at 0° from equation 3a into equation 6 one obtains

$$R_i' \text{ (at } 0°) = 3.07 \times 10^{-5}[Bz_2O_2][DMA] \quad (7)$$

Equation 7 is easy to interpret. Assuming that the efficiency of the initiation process is high and that it is independent of the $[Bz_2O_2]$ and [DMA], equation 7 suggests that radicals are produced from dimethylaniline and benzoyl peroxide by a bimolecular mechanism.

At the higher temperatures, however, calculation of $R_i$ from equations 6, 3 and 4 leads to the following result

$$R_i' = K'[Bz_2O_2]^a[DMA]^a \quad (8)$$

where $a$ has the values 0.79, 0.76, and 0.71 at the temperatures 30, 45 and 60°, respectively, and $K'$ also varies with the temperature. There is no obvious kinetic interpretation either of equations 3b, 3c or 3d nor of equation 8, and these equations will have to be regarded as empirical till further explanation is forthcoming.

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PRINCETON, N. J.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY OF LOUISIANA STATE UNIVERSITY]

# The Metal Complexes of Tris-anhydro-o-aminobenzaldehyde[1,2]

BY GUNTHER L. EICHHORN AND RASHID A. LATIF

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In a reaction analogous to the conversion of phthalonitrile to phthalocyanine, copper(II), nickel(II) and cobalt(II) ions react with *o*-aminobenzaldehyde to produce complexes of a trimeric condensate, tris-anhydro-*o*-aminobenzaldehyde. This coördinating agent, apparently quadridentate, is also formed by treatment with manganese(II) ion, but in this instance the isolated compound contains no complexed metal ion. Tris-anhydro-*o*-aminobenzaldehyde has the ability to stabilize low oxidation states, bringing about the reduction of copper(II) to copper(I), and preventing the oxidation of cobalt to the +3 state. The copper(I) complex is susceptible to oxidation or disproportionation, depending upon the conditions to which it is subjected.

## Introduction

Among the more important developments in the recent history of coördination chemistry has been the increasing recognition that complex formation does not necessarily occur through a simple additive process involving the components of the complex, but that indeed extensive modification may occur in either donor or acceptor as a consequence of coordinate covalent bond formation. A very familiar example of such modification is the tetramerization of phthalonitrile to phthalocyanine[3] under the influence of metals or metallic ions. The metal ion catalysis of the trimerization of *o*-aminobenzaldehyde may be considered analogous to this synthesis of phthalocyanine.

**Reaction of Metal Ions with *o*-Aminobenzaldehyde.**—The reaction between *o*-aminobenzaldehyde and metal ions has been previously carried out in the presence of ammonia, and has resulted in the formation of complexes of the aldimine derivative of the aldehyde.[4] In the present investigation ammonia was omitted from the reaction mixture in an attempt to secure the complexes of unaltered *o*-aminobenzaldehyde and to study the reaction of the latter with ethylenediamine and other amine derivatives. The nitrates of divalent copper, nickel, cobalt and manganese were employed. Analyses of the products of the reaction did not conform to calculated values for the *o*-aminobenzaldehyde complexes, but were in accord with the theoretical composition of complexes of the trimeric condensate of the molecule. The charge on the metal ion in the complexes was neutralized by uncoördinated

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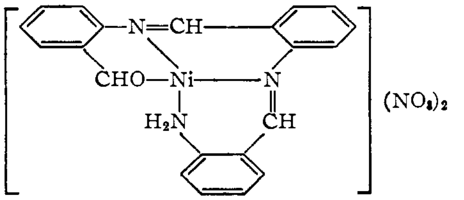
[1] Presented at the Regional Conclave of the American Chemical Society, New Orleans, December 10–12, 1953.

[2] Taken in part from the Ph.D. thesis of Rashid A. Latif, Louisiana State University, 1953.

[3] G. T. Byrne, R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, 1033 (1934).

[4] P. Pfeiffer, T. Hesse, R. Pfitzner, W. Scholl and H. Thielert, *J. prakt. Chem.*, **149**, 217 (1937).

nitrate ions. The structure of the nickel complex may, for example, be depicted as



The cobalt complex also involved two nitrate ions but the copper complex was associated with only one nitrate, indicating that copper had been reduced to the +1 state as a result of the coördination. The product isolated from the reaction with manganese ion did not contain any metal, but proved to be the pure tris-anhydro-*o*-aminobenzaldehyde.

A trimeric condensation product has been previously obtained from *o*-aminobenzaldehyde.[5,6] The physical properties (*e.g.*, melting point and solubilities) of our compound differ very markedly from those of the other substance; the structure of the latter[6] is apparently not the same as that of the trimer under consideration here.

**Oxidation States of the Metals in the Complexes.**—The number of nitrate ions in the compound may be taken as an indication of the oxidation state of the metal. Confirmation of this relationship was obtained through controlled potential electrolysis; the metal in the nickel complex required two electrons, and in the copper complex only one, for reduction to the elemental state.

Since copper is coördinated in the +1 state and cobalt in the +2 state, it may be concluded that tris-anhydro-*o*-aminobenzaldehyde stabilizes the lower oxidation state of metal ions. The reaction between *o*-aminobenzaldehyde and copper(II) is significant in that it involves a change in the nature of both metal ion and the coördinating agent as a result of the coördination.

**Oxidation of the Copper(I) Complex.**—When a dilute solution of the copper(I) complex is treated with base, the light yellow solution turns orange red; immediate addition of acid brings back the yellow color. If the orange red basic solution is allowed to stand in air for an hour, however, the solution becomes colorless, and then addition of acid produces no visible change. These observations may be interpreted by attributing the orange red color to a basic form of the copper(I) complex, and the colorless solution to the complete oxidation to copper(II). As long as some copper(I) remains, acidification causes reconversion to the yellow substance, but after complete oxidation has occurred, such a transformation is no longer possible. Addition of excess hydroxide to a *concentrated* solution of the copper(I) complex causes precipitation of a brown solid, stable in air, and readily soluble in acid, reforming the dissolved copper(I) complex. The precipitate is probably the hydroxide of the copper(I) complex.

**Disproportionation of the Copper(I) Complex.**—Another interesting reaction of the copper(I) complex was discovered accidentally. When a solution of the complex was prepared for electrolysis by placing it in contact with a mercury electrode and adding a potassium chloride electrolyte, a dark blue crystalline precipitate, containing copper(II), emerged from the solution. No such precipitation occurs in the absence of halide ion when the copper(I) complex nitrate is poured over mercury, although other halide or pseudohalide ions, *e.g.*, bromide, iodide and thiocyanate, may be substituted for chloride (only in the presence of metallic mercury, however). The two constituents that appear to be essential for the formation of the precipitate are metallic mercury and a halide or pseudohalide ion. The reaction may be considered a disproportionation of copper(I) into an insoluble copper(II) complex halide and copper(0) amalgam. When the nickel(II) complex is subjected to the same treatment under which the copper(I) complex disproportionates, it does not yield to the reaction, as indeed it should not, since nickel cannot be oxidized beyond the +2 state, except in very unusual circumstances.

**Stability of the Complexes.**—The copper(I) and nickel(II) complexes show no tendency to exchange indicating that they are very slightly dissociated. Spectrophotometric investigations demonstrate that the spectrum of the copper complex is unaffected by the presence of nickel ion, and *vice versa*. Moreover, solutions containing both complexes exhibit degrees of absorption that can be calculated from the concentrations of the component solutes.

Further evidence for the remarkable stability of these complexes arises from the fact that they will *not* react with ethylenediamine to produce Schiff's base complexes.

## Experimental

**Copper Complex of Tris-anhydro-*o*-aminobenzaldehyde.**—A 200-ml. three-necked round bottom flask was mounted on a steam-bath and fitted with mechanical stirrer, reflux condenser and a 50-ml. separatory funnel; 3.63 g. (0.03 mole) of *o*-aminobenzaldehyde, prepared according to directions from "Organic Syntheses,"[7] dissolved in 50 ml. of absolute ethyl alcohol, was introduced into the reaction flask, and 2.41 g. (0.01 mole) of copper(II) nitrate dihydrate dissolved in 50 ml. of absolute ethyl alcohol was poured into the separatory funnel. Stirring was initiated and the copper nitrate solution was added dropwise to the refluxing contents of the flask.

During the course of the heating the color of the reaction mixture changed from blue through yellow green to the deep olive green of the reaction product. After refluxing for six hours the mixture was transferred to a 100-ml. erlenmeyer flask and heated on a steam-bath until the volume had been reduced to approximately 20 ml. and a dark crystalline precipitate had formed. The mixture was then cooled and filtered through a fritted glass funnel. The precipitate was washed five times with absolute ethyl alcohol and ether, and allowed to dry at 25° for 24 hours, m.p. > 300°.

*Anal.*[8] Calcd. for $C_{21}H_{17}N_4O_4Cu$: C, 55.68; H, 3.78; N, 12.37. Found: C, 55.28; H, 3.31; N, 12.72.

**Nickel Complex of Tris-anhydro-*o*-aminobenzaldehyde.**—3.63 g. (0.03 mole) of *o*-aminobenzaldehyde and 2.91 g. (0.01 mole) of nickel (II) nitrate hexahydrate, both dissolved in 50 ml. of absolute ethyl alcohol, were mixed according to the procedure given in the above preparation. The color of the reaction mixture changed from light green to yellow after one hour of refluxing. At the end of the

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(5) F. Seidel, *Ber.*, **59B**, 1894 (1926).

(6) E. Bamberger, *ibid.*, **60B**, 314 (1927).

(7) L. I. Smith and J. W. Opie, *Org. Syntheses*, **28**, 11 (1948).

(8) All analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

preparation, which required eight hours, an orange crystalline precipitate had formed. This precipitate was washed and dried as above, m.p. > 300°.

*Anal.*[8] Calcd. for $C_{21}H_{17}N_5O_7Ni$: C, 49.44; H, 3.36; N, 13.73. Found: C, 51.63; H, 3.24; N, 13.82.

**Cobalt Complex of Tris-anhydro-*o*-aminobenzaldehyde.**—3.63 g. (0.03 mole) of *o*-aminobenzaldehyde and 2.91 g. (0.01 mole) of cobalt(II) nitrate hexahydrate, both dissolved in 50 ml. of absolute ethyl alcohol, were mixed as above. Refluxing was continued for 12 hours, during which time the color of the solution changed from pink to yellow brown. The solution was then transferred to an erlenmeyer flask and concentrated on a steam-bath, but no precipitate formed even when the volume had been reduced to 20 ml. The solution was cooled, and distilled water was added slowly; a brown precipitate began to form after the addition of a few ml. of water. When precipitation was complete, the addition of water was discontinued, the precipitate filtered, washed with water, redissolved in alcohol, and reprecipitated with water. Finally it was removed by filtration and dried in a vacuum desiccator for 24 hours, m.p. > 300°.

*Anal.*[8] Calcd. for $C_{21}H_{17}N_5O_7Co$: C, 49.42; H, 3.36; N, 13.72. Found: C, 50.21; H, 3.77; N, 13.92.

**Trimerization of *o*-Aminobenzaldehyde with Manganese(II) Ion.**—3.63 g. (0.03 mole) of *o*-aminobenzaldehyde and 2.87 g. (0.01 mole) of manganese(II) nitrate, both dissolved in 50 ml. of absolute alcohol, were mixed and treated according to the procedure for the preparation of the cobalt complex. A light yellow precipitate formed after the addition of water to the cooled alcoholic solution. The precipitate was filtered, washed with water, redissolved and reprecipitated several times, and finally filtered, and dried in a vacuum desiccator for 24 hours at 25°, m.p. 138–140°.

*Anal.*[8] Calcd. for $C_{21}H_{17}N_3O$: C, 77.04; H, 5.24; N, 12.48. Found: C, 77.20; H, 5.42; N, 11.58.

**Comparison of Properties of Monomeric and Trimeric *o*-Aminobenzaldehyde.**—Monomeric *o*-aminobenzaldehyde ($C_7H_7NO$) is a slightly yellow compound that melts at 39–40° and decomposes before boiling. It is very soluble, in alcohol, ether, acetone and aniline, slightly soluble in chloroform, carbon tetrachloride and benzene, and very slightly soluble in water. It reacts with concentrated mineral acids with the evolution of a gas and the formation of an orange solution. The addition of dilute acids changes the color of the organic compound to pink, but further addition of concentrated acid ultimately brings about solution. No reaction is observed with ammonium hydroxide and with alkali in the cold.

The trimeric condensate ($C_{21}H_{17}N_3O$) is also yellow, and melts at 138–140°. It is very soluble in alcohol, acetone, chloroform, aniline and benzene, slightly soluble in ether and carbon tetrachloride, and insoluble in water. Its behavior toward mineral acids, ammonia and alkali resembles that of the monomer.

**Attempted Trimerization of *o*-Aminobenzaldehyde in the Absence of Metal Ions.**—A solution of the monomeric aldehyde in alcohol was subjected to the same conditions that caused the formation of the trimer in the presence of the metal ions; the latter were, however, omitted in this experiment. The addition of water to the reaction product did not yield any precipitate, thus indicating that no trimerization had taken place.

**Electrolysis of Copper and Nickel Complexes.**[9]—The setup used for the constant potential electrolysis was similar to that described by Lingane,[10] but modified by separating the reference electrode from the cell by means of an agar-lithium sulfate bridge. This bridge was surrounded by a concentric tube of larger diameter drawn out to a capillary at the end approaching the mercury cathode. The purpose of the bridge was to prevent diffusion of chloride ions from the reference electrode into the cell, and thus to avoid the disproportionation reaction which would then ensue in the presence of mercury.

When the electrolysis apparatus had been assembled, mercury was introduced into the cell until the platinum wire cathodic lead was completely covered by it. Thereupon 100 ml. of solution, $5 \times 10^{-4}$ *M* in the complex to be analyzed and $5 \times 10^{-2}$ *M* in lithium sulfate, was placed in the cell on top of the mercury. Nitrogen was then bubbled through the solution for 30 minutes to remove the dissolved oxygen. The stirrer was started, and the tip of the bridge from the reference electrode was adjusted so that it just touched the mercury surface. The gas coulometer was filled with 0.5 *M* potassium sulfate solution, which had been previously saturated with an oxygen–hydrogen gas mixture. The coulometer was connected to the cell, and a potential difference applied and adjusted until the potential of the mercury cathode reached the value at which the operation was to be carried out. The electrolysis was discontinued when the current became negligibly small, and the volume of the oxygen–hydrogen mixture was recorded, after the solution remaining in the coulometer had been leveled with that in the bulb.

The apparatus and technique were checked by electrolyzing a solution of copper(II) sulfate at a cathode potential of −0.5 volt. The volume of the gas mixture, corrected for temperature and pressure, was in agreement with the theoretical value for two electron reduction.

The electrolysis of the copper and nickel complexes was then carried out at a cathodic potential of −1.78 volts. The operation was concluded after four hours, when the current had dropped to about 0.01 milliampere, and negligible quantities of mixed gases were evolving in the coulometer. The results are gathered in Table I. Assuming that the oxidation state of nickel is +2, four electrons are required in a partial reduction of the coördinating agent. Since five electrons are involved in the reduction of the copper complex, the oxidation state of +1 has been confirmed.

TABLE I

ELECTROLYSIS EXPERIMENTS

| Soln. (100 ml. $5 \times 10^{-4}$ *M*) | Applied pot., volts | Vol. of mixed $H_2$–$O_2$ gases (ml. at S.T.P.) Theoret. | Found | No. of electrons reduced |
|---|---|---|---|---|
| $CuSO_4$ | −0.5 | 1.68 | 1.51 | 2 |
| Cu complex | −1.78 | 4.20 | 4.05 | 5 |
| | | | 4.01 | |
| Ni complex | −1.78 | 5.04 | 4.82 | 6 |
| | | | 4.80 | |

**Reaction of the Copper(I) Complex with Halide Ion and Metallic Mercury.**—Fifty ml. of a solution containing 0.001 *M* copper(I) complex and 0.1 *M* sodium chloride was shaken vigorously with 20 g. of metallic mercury, and permitted to stand in contact with the mercury for 48 hours. The solution, which at this time contained a blue precipitate, was removed from the mercury by decantation, and the precipitate was thereupon removed from the solution by filtration. The precipitate was washed with water and analyzed.[8]

*Anal.* Calcd. for $C_{21}H_{19}O_3N_3Cl_2Cu_2$[11]: C, 45.0; H, 3.4; N, 7.5. Found: C, 44.66; H, 3.37; N, 6.94.

Solutions of this complex in organic solvents, unlike solutions of the copper(I) complex, oxidize potassium iodide solutions to iodine.

The mercury was cleaned thoroughly and subjected to spectrographic analysis (using pure mercury as a control), verifying the presence of dissolved copper in the mercury.[12]

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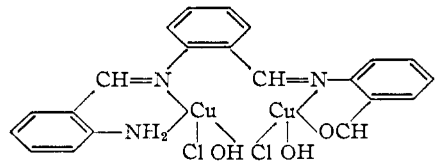
[9] The authors are indebted to Dr. Paul Delahay and Dr. George Stiehl for valuable aid during the course of these investigations.

[10] J. J. Lingane, THIS JOURNAL **67**, 1916 (1945).

[11] The following structure may account for this elemental analysis.



[12] The spectrographic analysis was performed by Mr. Loys J. Nunez, Jr., Mr. Horace Ory, and Mr. Farris Mitchell.