$$Cr(H_2O)_5{}^{3+} + H_2O \xrightarrow{k_{H_2O}} Cr(H_2O)_6{}^{3+}$$

This mechanism accounts for the observed retardation: if the steady-state condition $d[Cr(H_2O)_5{}^{3+}]/dt = 0$ is assumed, it follows that

$$-\frac{d[CrI^{2+}]}{dt} = k_{H_2O}[Cr(H_2O)_5{}^{3+}] =$$

$$\frac{k_{H_2O}k_0}{k_I[I^-] + k_{H_2O}} [CrI^{2+}] = k[CrI^{2+}]$$

Hence, the rate constant $k$ is decreased by iodide. This effect will be negligible only if $k_I[I] \ll k_{H_2O}$; this condition is realized in expt. 1–3 and 8–11, where the iodide concentration is smaller than $5 \times 10^{-3}$ $M$. The results of expt. 4–7 were used to evaluate $k_I/k_{H_2O}$: the plot of $1/k$ vs. $[I^-]$ yields a straight line. The quantity $1/k_0$ measured from the graph is equal to $1/k_0$ measured in perchloric acid ($1.52 \times 10^{-4}$ sec.$^{-1}$). The ratio $k_I/k_{H_2O}$ is equal to 0.24.

**The Reaction in the Presence of Chloride.**—The equilibrium quotient $Q = [CrCl^{2+}]/[Cr^{3+}][Cl^-]$ is equal to 0.086 at 30° and an ionic strength of 0.959.[16] Hence the equilibrium ratio is $R_{eq} \sim 0.086$ under the conditions of expt. 8. Formation of $CrCl^{2+}$ during the decomposition of $CrI^{2+}$ cannot be attributed to the anation of $Cr(H_2O)_6{}^{3+}$, since this reaction is much too slow—the second-order rate constant[16] is $\sim 1.6 \times 10^{-7}$ l. mole$^{-1}$ sec.$^{-1}$ under the conditions of expt. 8. It has been shown[8] that this reaction is not catalyzed by the decomposition products of $CrI^{2+}$, hence it was concluded that in this case, as in the presence of

bromide, $CrCl^{2+}$ is formed by direct substitution of iodide.

Replacement of perchlorate by chloride causes a slight but significant increase in the decomposition rate of $CrI^{2+}$ (6.5% in hydrochloric acid, 1 $M$). This specific effect of chloride may be due to the existence of ion pairs which weaken the Cr–I bond. Alternatively, the effect might be attributed to a small contribution of a bimolecular reaction path. Even if the latter assumption is made, the expected product ratio $[CrCl^{2+}]/[Cr(H_2O)_6{}^{3+}]$ should be less than 0.065 at $[Cl^-] = 1$ while the experimental value is 0.143. An SN2 reaction path could not account for the greater portion of $CrCl^{2+}$ produced in the reaction, and it is necessary to assume an SN1 mechanism similar to that operating in bromide solutions. Experiments 8–11 reveal that the dependence of the product ratio on $[Cl^-]$ and $[H^+]$ is similar to that found in bromide solutions. No correction for aquation of $CrCl^{2+}$ is necessary because of the low rate of this reaction[16]—the first-order rate constant is $\sim 13 \times 10^{-7}$ sec.$^{-1}$. The ratios $k_{Cl}/k_{H_2O}$ were calculated by assuming that the reaction proceeds solely by an SN1 mechanism.

Comparison of the ratios $k_X/k_{H_2O}$ for chloride, bromide, and iodide (Table II) reveals that these ions do not differ considerably in their ability to compete with water for the intermediate $Cr(H_2O)_5{}^{3+}$.

The effect of anions on the decomposition of $CrBr^{2+}$ and $CrCl^{2+}$ is now being investigated, by following the method outlined here.

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# Synthesis of Chelating Agents. III.[1] Chelating Behavior of Keto Derivatives of Iminodiacetic Acids

By TAKESHI ANDO AND KEIHEI UENO

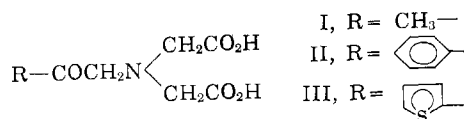ω-Aminoacetophenone-N,N-diacetic acid (AAPDA) and 2-glycylthiophene-N,N-diacetic acid (GTDA) have been synthesized and the stoichiometric stability constants of their proton and metal complexes have been measured potentiometrically at 25° in a medium of constant ionic strength of 0.10 $M$. The 1:1 chelates of both ligands show nearly the same stability for the metal ions chosen, and the order of relative stabilities is Cu(II) > Ni(II) > Cd(II) ≈ Zn(II) > Co(II) > Ca(II) > Sr(II) > Mg(II). The formation of 1:2 chelates is also observed for Cu(II), Ni(II), Cd(II), Zn(II), and Co(II). By comparing their stability constants with those of aminoacetone-N,N-diacetic acid (AADA), the formation of a stronger coordination bond with carbonyl oxygen is suggested for AAPDA and GTDA than for AADA.

## Introduction

In the previous paper[1] the synthesis and the chelating behavior of aminoacetone-N,N-diacetic acid (AADA) (I) have been reported, and it was proved that the carbonyl oxygen of the ligand contributed to the coordination for a certain group of metal ions.

(1) Paper II: T. Ando, *Bull. Chem. Soc. Japan*, **36**, 1593 (1963).

In the present investigation, ω-aminoacetophenone-N,N-diacetic acid (AAPDA) (II) and 2-glycylthiophene-N,N-diacetic acid (GTDA) (III) have been synthesized and their chelating behaviors investigated in order to understand the effect of the substitution of the methyl group α to the carbonyl carbon atom with aromatic rings.

$$R-COCH_2N\left\langle \begin{array}{l} CH_2CO_2H \\ CH_2CO_2H \end{array} \right. \qquad \begin{array}{l} I, \ R = CH_3- \\ II, \ R = \langle \bigcirc \rangle - \\ III, \ R = \langle \bigcirc \rangle_S - \end{array}$$

AAPDA and GTDA were synthesized in a manner similar to the synthesis of AADA, and the chelate stability measurements were carried out by the pH titration method on solutions of 1:1 and 1:2 metal: ligand ratio for metal ions such as copper(II), nickel(II), zinc(II), cadmium(II), cobalt(II), calcium(II), strontium(II), and magnesium(II).

The stability constant measurements indicate that the coordination of carbonyl oxygen in AAPDA and GTDA is more pronounced than in AADA. This stabilization effect by the aromatic ring substitution may be explained by the $+M$ effect of the aromatic ring against the carbonyl oxygen.

## Experimental

**Synthesis of AAPDA (II).**—The preparation of AAPDA was carried out in a manner similar to that of AADA (I).[1] A benzene solution (150 ml.) containing 11 g. (0.055 mole) of $\omega$-bromoacetophenone[2] and 20 g. (0.124 mole) of iminodiacetic acid dimethyl ester[3] was refluxed at 50–70° for 4 hr. After cooling, the precipitate of iminodiacetic acid dimethyl ester hydrobromide was filtered off and was washed with 50 ml. of benzene.

The combined filtrate and wash was concentrated under reduced pressure. The residue, a pale yellow oil, was dissolved into 70–80 ml. of ethanol, and the solution was subjected to hydrolysis with addition of 50 ml. of 5% NaOH for 2 hr. with occasional shaking at 50–60°. After concentrating the solution to about 50 ml., the pH of the cooled residue was adjusted to about 2 with concentrated hydrochloric acid in order to effect the precipitation of AAPDA. The crude product was filtered off and washed with 50% ethanol, then with ether; yield 12 g. (80%). The pure acid, obtained by repeated recrystallization from hot water, is in the form of white needles; it decomposes at 169–170°. The pure material has 0.5 mole of water of crystallization, which can only be removed by drying it over phosphorus pentoxide under vacuum for 24 hr.

*Anal.*[4] Calcd. for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.21; N, 5.58. Found: C, 57.40; H, 5.26; N, 5.48.

Pure AAPDA is slightly soluble in water (about 1.3 g./1000 ml.) and soluble in hot ethanol, methanol, dioxane, and acetone. It is insoluble in benzene and ether.

**Synthesis of GTDA (III).**—Iminodiacetic acid dimethyl ester[3] (10.5 g., 0.065 mole) was added to 50 ml. of an anhydrous ether solution of 2-bromoacetylthiophene which was prepared from 4.3 g. (0.034 mole) of 2-acetylthiophene and 5.6 g. of bromine (0.035 mole). As 2-bromoacetylthiophene was very unstable, it was prepared as needed by the bromination of 2-acetylthiophene in a manner similar to the $\omega$-bromination of 1-acetonaphthone.[5] During the addition, the mixture was kept below 10° under a nitrogen atmosphere; then it was left to stand for 2 days at 0–5°. After evaporation of the ether under reduced pressure, the residue was extracted with hot benzene. The crude GTDA dimethyl ester was obtained from benzene solution after evaporating the solvent under reduced pressure. The pure ester, after recrystallization from ether, was in the form of white prisms and melted at 71–72°.

*Anal.*[4] Calcd. for $C_{12}H_{15}NO_5S$: C, 50.51; H, 5.30; N, 4.91. Found: C, 50.64; H, 5.58; N, 4.91.

The free acid of GTDA was prepared by the hydrolysis of pure dimethyl ester with 5% sodium hydroxide at room temperature, followed by acidification with hydrochloric acid; yield 4 g. (46%).

The pure product was obtained by repeated recrystallization from 10% ethanol. It was in the form of white bulky needles and decomposed at 183–187°.

*Anal.*[4] Calcd. for $C_{10}H_{11}NO_5S$: C, 46.68; H, 4.31; N, 5.45. Found: C, 46.51; H, 4.35; N, 5.39.

GTDA is slightly soluble in water (about 1.0 g./1000 ml.). The solubilities in various solvents are similar to those of AAPDA.

It is interesting to note that the infrared spectra of GTDA taken after one or two recrystallizations differ from those taken on a sample of the higher stage of recrystallization. Since the elementary analytical data for both samples were identical, the spectral difference may be caused by a different modification of crystalline structure. The result of a more detailed investigation of this finding will be reported elsewhere.

**Measurements.**—The experimental method and the conditions employed in this study are the same as those described in the previous paper.[1] The concentrations of the metal and ligand are about $1 \times 10^{-3}$ $M$ in runs for which the ratio of metal ion to ligand concentration was 1:1, while the concentration of the ligand was about $2 \times 10^{-3}$ $M$ in runs where the ratio was 1:2. The metal ions chosen were copper(II), nickel(II), zinc(II), cadmium(II), cobalt(II), strontium(II), calcium(II), and magnesium(II).

Alkaline earth metal chelates were measured only in runs of 1:1 ratio. The stock solutions of the two ligands were preserved in a refrigerator, because they are not stable indefinitely at room temperature.

**Calculations.**—The equilibrium constants described in this paper are summarized as follows.

$$pK_1 = -\log \frac{[HA^-][H^+]}{[H_2A]} \qquad pK_2 = -\log \frac{[A^{2-}][H^+]}{[HA^-]}$$

$$K_{MA} = \frac{[MA]}{[M^{2+}][A^{2-}]} \qquad K_{MA_2} = \frac{[MA_2^{2-}]}{[MA][A^{2-}]}$$

where $H_2A$ and M represent the free acid of the ligand and the metal ion, respectively.

The acid dissociation constants were calculated by an algebraic method as it was considered that each stage of acid dissociation occurred separately, and results were checked by a modified Bjerrum method.

The stability constants of the transition metal chelates were evaluated by the least-squares method,[6–8] using the data from 1:2 titrations. The equation employed for this method is[6]

$$\frac{\bar{n}}{(\bar{n}-1)[A^{2-}]} = \frac{(2-\bar{n})[A^{2-}]}{(\bar{n}-1)} K_{MA}K_{MA_2} - K_{MA}$$

where $\bar{n}$ is the average number of ligand molecules or ions bound per metal ion present. Now, if one simplifies the above equation by replacing each term as

$$A = -K_{MA}$$

$$B = K_{MA}K_{MA_2}$$

$$Y = \bar{n}/(\bar{n}-1)[A^{2-}]$$

$$X = (2-\bar{n})[A^{2-}]/(\bar{n}-1)$$

then, the equations for the least-squares method can be written

(2) R. M. Cowper and L. H. Davidson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 480.

(3) J. V. Dubsky, *Ber.*, **50**, 1694 (1917).

(4) Elementary analyses were carried out by Mr. Michio Shido of the Elementary Analysis Center of Kyushu University.

(5) T. L. Jacobs, S. Winstein, J. W. Ralls, J. H. Robson, R. B. Henderson, R. I. Akawie, W. H. Florsheim, D. Seymour, and C. A. Seil, *J. Org. Chem.*, **11**, 21 (1946).

(6) H. Irving and H. S. Rossotti, *J. Chem. Soc.*, 3397 (1953).

(7) F. J. C. Rossotti and H. S. Rossotti, "The Determination of Stability Constants," McGraw-Hill Book Co., New York, N. Y., 1961.

(8) Such calculations were carried out at the Computing Center of Kyushu University.

$$\Sigma Y = nA + B\Sigma X$$

$$\Sigma XY = A\Sigma X + B\Sigma X^2$$

where $n$ represents the number of observed points employed for each set of calculations. For the alkaline earth metal chelates, the conventional algebriac method was employed using the data from 1:1 titration.

As it was thought that the least-squares method gave more reliable results than Bjerrum's method, the stability constants of AADA–transition metal chelates[1] were also recalculated by the least-squares method for the purpose of comparison.

## Results and Discussion

The titration curves of AAPDA and GTDA were found to be almost similar. The stoichiometric acid dissociation constants and chelate stability constants for AAPDA and GTDA, as well as AADA, are summarized in Table I.[9]

TABLE I
EQUILIBRIUM CONSTANTS OF KETO DERIVATIVES OF
IMINODIACETIC ACID AT 25°, $\mu = 0.10$ (KNO₃)

|  | AADA(I) $pK_1 = 2.62$, $pK_2 = 7.71$ | | AAPDA(II) $pK_1 = 1.9$, $pK_2 = 7.89$ | | GTDA(III) $pK_1 = 1.95$, $pK_2 = 7.46$ | |
| Metals | log $K_{MA}$ | log $K_{MA_2}$ | log $K_{MA}$ | log $K_{MA_2}$ | log $K_{MA}$ | log $K_{MA_2}$ |
| --- | --- | --- | --- | --- | --- | --- |
| Cu(II) | 9.10 | 4.88 | 9.22 | 5.03 | 8.79 | 5.31 |
| Ni(II) | 7.43 | 5.27 | 8.12 | 5.72 | 8.14 | 5.78 |
| Zn(II) | 6.89 | 3.83 | 7.13 | 3.97 | 7.35 | 4.26 |
| Cd(II) | 6.77 | 4.13 | 7.37 | 4.97 | 7.43 | 4.93 |
| Co(II) | 6.37 | 4.50 | 6.99 | 4.85 | 6.93 | 4.97 |
| Ca(II) | 4.08 | ... | 4.11 | ... | 4.26 | ... |
| Sr(II) | 3.62 | ... | 3.24 | ... | 3.40 | ... |
| Mg(II) | 2.72 | ... | 3.06 | ... | 2.80 | ... |

With regard to the acid dissociation constants, it is noteworthy that the acidities of the first dissociation steps of AAPDA and GTDA are stronger than that of AADA, while the acidities of the second dissociation steps of AAPDA and GTDA are nearly the same as that of AADA. Since the values of $pK_1$ of AAPDA and GTDA are nearly the same as those of the typical derivatives of methyliminodiacetic acid, the $pK_1$ value of AADA may be considered exceptionally high.

As shown in Table I, the stability constants of AAPDA are nearly the same as those of GTDA, and replacement of the methyl group of AADA with the aromatic ring results in an increase of the metal chelate stability with the exception of strontium. The stability orders of the 1:1 chelates of the three ligands for the metal ions investigated are found to be the same, and they are in the order Cu(II) > Ni(II) > Cd(II) ≈ Zn-(II) > Co(II) > Ca(II) > Sr(II) > Mg(II). This order is also observed for acetoamidoiminodiacetic acid,[10] which also has a carbonyl oxygen as an additional coordinating site. This order is characteristic in that the stability for cadmium(II) is unusually high compared with those for zinc(II) and cobalt(II).

(9) The experimental data for these titrations have been deposited as Document No. 8198 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $5.00 for photoprints or $2.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(10) G. Schwarzenbach, G. Anderegg, W. Schneider, and H. Senn, *Helv. Chim. Acta*, **38**, 1147 (1955).

As discussed for AADA in our previous paper,[1] it is likely that the carbonyl oxygens of AAPDA and GTDA are also involved in the coordination to the metal ions. The extent of the contribution of carbonyl oxygen to the 1:1 chelate stability of iminodiacetic acid derivatives can be estimated by the linear correlation method,[10] and the increased stabilities of AAPDA and GTDA due to the coordination of carbonyl oxygen were estimated for selected metal ions, and they are shown in Table II in terms of $\Delta \log K_T$ along with the values for AADA.

TABLE II
INCREASED STABILITIES OF KETO DERIVATIVES OF
IMINODIACETIC ACID DUE TO THE COORDINATION
OF CARBONYL OXYGEN

| Metal ion | $\Delta \log K_T$ for AADA | AAPDA | GTDA |
| --- | --- | --- | --- |
| Cu(II) | −0.1 | −0.2 | −0.1 |
| Ni(II) | +1.0 | +1.5 | +1.9 |
| Zn(II) | +1.1 | +1.1 | +1.8 |
| Cd(II) | +2.2 | +2.4 | +2.9 |
| Co(II) | +0.8 | +1.2 | +1.6 |
| Ca(II) | +1.3 | +1.2 | +1.6 |
| Sr(II) | +1.8 | +1.3 | +1.8 |
| Mg(II) | +0.2 | +0.5 | +0.4 |

It is clear from Table II that the chelating tendencies of AAPDA and GTDA are similar to that of AADA, and that the carbonyl oxygen of AAPDA and GTDA also participates in the coordination with metal ion. In the case of transition metals, with the one exception of copper(II), the stabilization effect is more distinct in AAPDA and GTDA than in AADA. It is self-explanatory that no stabilization effect is observed for copper ion in all cases, because the square-planar configuration of cupric ion does not favor the coordination of the carbonyl oxygen of the ligands.

The increased stabilization effect by the aromatic ring substitutions may possibly be caused by a +M effect of aromatic rings. The infrared spectra of AADA, AAPDA, and GTDA show a carbonyl band at 1715, 1685, and 1670 cm.⁻¹, respectively. The lowering of the frequency of the carbonyl band is understood to be due to the decrease of the double bond character of the C=O bond through the conjugation of the carbonyl group with the aromatic ring. This effect will result in an increase of electron density on the carbonyl oxygen, and the coordination of the carbonyl group to the metal ion becomes more favorable for AAPDA and GTDA than for AADA. This explanation is also supported by the fact that the order of the magnitude of the infrared shift is consistent with the order of the increased stabilization effect. However, more experimental data may be needed to draw a conclusive answer.

The reason for the very small stabilization effect for magnesium ion compared with calcium and strontium may be the smaller ionic radius of magnesium. The ionic radius is so small that the carbonyl oxygen cannot coordinate to the central metal ion because of the overcrowding of the coordinating groups around magnesium ion.

It is also interesting to note that the over-all stability constants (log $K_{MA}$ + log $K_{MA_2}$) of AAPDA and GTDA for cadmium are higher than those for zinc, although the stabilities of their 1:1 cadmium chelates are nearly the same as those of their zinc chelates. Such strong affinity for cadmium has been reported for a very limited number of ligands such as catechol-$O',O'$-diacetic acid[11] or bis(2-aminoethyl ether)-N,N,-N',N'-tetraacetic acid.[12]  Since all of these ligands have the coordinating oxygen, it is quite probable that their unusual affinity for cadmium ion is related to the coordination of oxygen to the metal ion.

(11)  T. Hatsutori, K. Suzuki, and K. Yamasaki, Abstracts of Papers, 12th Symposium on Coordination Chemistry sponsored by the Chemical Society of Japan, Tokyo, 1962, p. 115.
(12)  J. H. Holloway and C. N. Reilly, *Anal. Chem.*, **32**, 249 (1960).

CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY,
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# Metal Chelates of Mercaptosuccinic and α,α'-Dimercaptosuccinic Acids[1]

BY G. R. LENZ AND A. E. MARTELL

The interaction of metal ions with α-mercaptosuccinic acid and with α,α'-dimercaptosuccinic acid has been determined by potentiometric measurement of hydrogen ion concentration.  With mercaptosuccinic acid, evidence is presented for the formation of complexes having 1:1 and 2:1 molar ratios of ligand to metal, as well as for zinc and nickel hydroxo complexes. For α,α'-dimercaptosuccinic acid, the existence of 1:1 and 2:1 complexes is established together with various protonated and hydroxo complexes.  Equilibrium constants are reported for soluble metal chelate systems, and the equilibrium data are interpreted in terms of the probable structure of the complexes formed.

## Introduction

The ligand α,α'-dimercaptosuccinic acid, DTTA, is of special interest as a sequestering agent for metal ions, since it has two mercapto groups available for chelate ring formation.  In order to study this reagent the potentiometric studies of Agren and Schwarzenbach[2] were extended to additional metal ions.  For comparison and as a possible means of providing a better understanding of the properties of α,α'-dimercaptosuccinic acid, the analogous α-mercaptosuccinic acid, TMA, was studied with a variety of metal ions, considerably extending the previous work of Cheney, *et al.*[3]

## Experimental

**Reagents.**—A sample of α-mercaptosuccinic acid (TMA), purchased from Evans Chemetics, Inc., New York, N. Y., was certified to be 99.67% pure and was used without further purification. The pure *meso*-α,α'-dimercaptosuccinic acid was purchased from Dojindo and Co., Kumamotoshi, Japan, and had been synthesized by the method of Gerecke, *et al.*[4]  The mercaptosuccinic acid melted at 152–153°, lit. 148°,[5] 149–150°,[6] 153–154°,[7] and the α,α'-dimercaptosuccinic acid softened at 194°, lit. 190–191°,[7] 210–211°,[4] and decomposed at 207–211°.

A sulfur analysis of α,α'-dimercaptosuccinic acid by Micro-Tech Laboratories, Skokie, Ill., gave 35.10% calculated, 35.87, 35.72% found.  Both ligands were standardized by potentiometric titration, using standard carbonate-free sodium hydroxide. The quality of the titration curves affirmed the high purity of the

ligands indicated above.  Metal ion solutions were prepared from Fisher reagent grade metal nitrates except for Mn(II) and Hg(II), which were obtained as the sulfate and chloride, respectively. The metal salt solutions were standardized by titration with ethylenediaminetetraacetic acid by standard methods.

**Potentiometric Measurements.**—Measurements of hydrogen ion concentration were carried out in a 100-ml. jacketed titration cell, which was fitted with a magnetic stirrer and a tightly-fitting rubber stopper through which were inserted nitrogen inlet and outlet tubes, a microburet delivery tube, and glass and calomel extension electrodes.  A Beckman Model GS pH meter was used to determine hydrogen ion concentrations.  The electrodes were calibrated by comparing the meter reading during the titration of standard acetic acid under the same experimental conditions with hydrogen ion concentrations calculated from the data tabulated by Harned and Owen.[8]  In the pH regions below 3.5 and above 10.5, the pH meter was calibrated by adding known amounts of hydrochloric acid and sodium hydroxide, respectively.  All potentiometric titrations and calibrations were made at 25.05 ± 0.05° and at an ionic strength adjusted to 0.10 $M$ (or in some cases 1.0 $M$) with potassium nitrate.

## Calculations

All calculations were made with the aid of an IBM 1620 computer at the Computation Center of Illinois Institute of Technology, using programs written by G. R. L.  To ensure accuracy, individual spot calculations were made for each equation.

**Acid Dissociation Constants.**—The acid dissociation constants of TMA and DTTA were calculated by a combined algebraic–geometric method.  The equilibria and dissociation constants involved are

$$K^H_j = \frac{[\mathrm{H}^+][\mathrm{H}_{n-j}\mathrm{L}]}{[\mathrm{H}_{n-j+1}\mathrm{L}]}$$

(1)  This work was supported by the U. S. Atomic Energy Commission under Grant No. AT(11-1)-1020.
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(3)  G. E. Cheney, Q. Fernando, and H. Freiser, *J. Phys. Chem.*, **63**, 2055 (1959).
(4)  M. Gerecke, E. A. H. Friedheim, and A. Brossi, *Helv. Chim. Acta*, **49**, 955 (1961).
(5)  E. Bilman, *Ann.*, **339**, 351 (1905).
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