in Pentane: Additional Comments.—It is to be noted that no evidence for such redistribution of $RSn(CH_3)_3$ to $(CH_3)_4Sn$ and $R_2Sn(CH_3)_2$ was found in those reactions where $(CH_3)_3SnBr$ was added to cyclopropyllithium in pentane, where the lithium reagent had been obtained by the transmetalation procedure (see experiments above). Apparently such redistribution occurs with facility in the case in question only in diethyl ether solution.

Acknowledgments.—The authors are grateful to the National Science Foundation for support of this work under Grant NSF G-21051 and to the Allied Chemical Corporation for a predoctoral fellowship to H. M. C. Thanks are due to the Metal & Thermit Corporation for gifts of organotin chemicals.

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Magnetic Properties and Thermochromism of Copper(II) Complexes with N-Alkylethylenediamines

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Received December 5, 1962

The magnetic and spectral properties of both the red and blue forms of bis-(N,N-diethylethylenediamine)-copper(II) perchlorate have been investigated, and possible mechanisms for the thermochromism have been considered. The antiferromagnetic character of some binuclear copper complexes of the general formula $[Cu_2(OH)_2(amine)_2](ClO_4)_2$ has been established, and the energy differences between the singlet and triplet states have been measured.

In 1938, Pfeiffer and Glaser[2] published the results of their investigations of the donor properties of some N-alkylethylenediamines toward copper(II) perchlorate. With N-methyl-, N,N′-diethyl-, and N,N-diethylethylenediamine, complexes of the general formula $[Cu(ligand)_2](ClO_4)_2$ were formed. However, with more alkyl substitution, *i.e.*, with N,N-diethyl-N′-methyl- and N,N,N′-triethylethylenediamine, complexes with the unusual composition Cu(amine)(OH)-(ClO_4) were isolated. Pfeiffer and Glaser[2] formulated these compounds as binuclear copper complexes with hydroxy bridges. The steric requirements of the N-alkyl groups which govern the formation of the binuclear complexes have been demonstrated.[3,4]

The bis-(N,N-diethylethylenediamine)-copper(II) perchlorate was found to exhibit an especially interesting property in that it is brick red at room temperature and blue above 44°. Pfluger and Eihausen[5] have shown that a change in the crystal form from triclinic to monoclinic accompanies the color change. Pfeiffer and Glaser[2] also reported that μ-dihydroxy-bis-(N,N-diethyl-N′-methylethylenediamine)-dicopper(II) perchlorate which is blue at room temperature has a blue to red transition between −100 and −120°.

We now wish to report the results of our magnetic and spectral investigations of some of these compounds.

Experimental

Preparation of the Compounds.—The compounds were prepared by Pfeiffer and Glaser's method,[2] purified by recrystallization, and analyzed to establish their purity.

In addition to the perchlorate salt of bis-(N,N-diethylethylenediamine)-copper(II) the NO_3^-, ClO_3^-, IO_4^-, IO_3^-, BrO_3^-, I^-, Cl^-, Br^-, PF_6^-, BF_4^-, CN^-, SCN^-, CO_3^{2-}, SO_4^{2-}, SiF_6^{2-}, OH^-, and *o,p*-dinitrobenzenesulfonate salts were prepared and checked for thermochromism. All of these compounds except the NO_3^- and SCN^- salts were blue at room temperature and did not change color when cooled in a liquid nitrogen bath. The red NO_3^- salt and the green SCN^- salt also did not exhibit thermochromism.

Magnetic Susceptibility Determinations.—The magnetic susceptibilities were determined by the method that has been described previously[6] using $Hg[Co(CNS)_4]$ as a standard.[7]

Spectral Studies.—The reflectance spectra were obtained with a Bausch and Lomb spectrophotometer equipped with the standard reflectance attachment. For the high temperature spectrum the sample was mounted on a block in which a heating element was embedded. Reagent grade magnesium carbonate was used as a standard.

The infrared spectra of salts intimately ground with mineral oil were obtained with a Beckman IR7 spectrophotometer equipped with a thermostated sample compartment.

Results

The reflectance spectra of bis-(N,N-diethylethylenediamine)-copper(II) perchlorate were recorded for both the high temperature and low temperature forms and are shown in Fig. 1. The maximum of the band in the spectrum of the high temperature form is shifted 30 mμ to the red, *i.e.*, from 490 to 520 mμ, with respect to the band in the spectrum of the low temperature form.

The temperature dependence of the magnetic susceptibility of bis-(N,N-diethylethylenediamine)-copper(II) perchlorate was determined. The diamagnetic correction was calculated from Pascal's constants.[8] There was no discontinuity or change in slope of the plot of the reciprocal of the corrected magnetic sus-

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[1] (a) Alfred P. Sloan Foundation Fellow; (b) Undergraduate Research Participant, N. S. F. Summer Program, 1961.

[2] P. Pfeiffer and H. Glaser, *J. prakt. Chem.*, [2] **151**, 134 (1938).

[3] F. G. Mann and H. R. Watson, *J. Chem. Soc.*, 2772 (1958).

[4] F. Basolo and R. K. Murmann, *J. Am. Chem. Soc.*, **74**, 5343 (1952); *ibid.*, **76**, 211 (1954).

[5] C. E. Pfluger and J. W. Eihausen, private communication; the space group in the high temperature form is C2/c with $Z = 4$. A complete crystal structure determination is in progress.

[6] W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Am. Chem. Soc.*, **85**, 265 (1963).

[7] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[8] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 403.

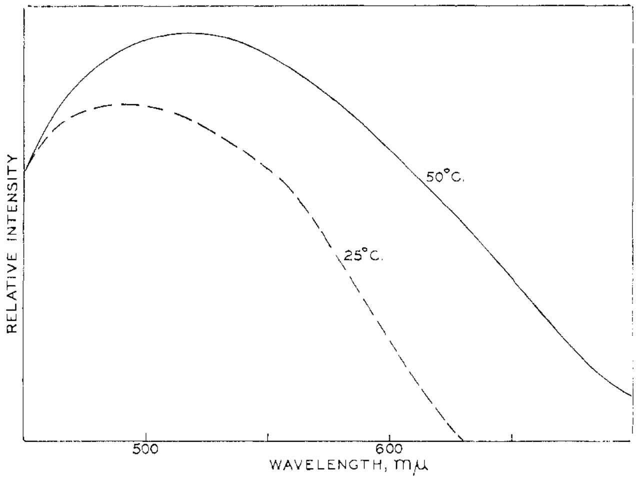

Fig. 1.—Reflectance spectrum of bis-(N,N-diethylethylenediamine)-copper(II) perchlorate; 25°, red form; 50°, blue form.

ceptibility *vs.* temperature near the color transformation temperature, or for that matter in the temperature range 77–344°K.; the precision of our measurements was ±0.5%. The magnetic moment was calculated from $\mu_{\text{eff}} = 2.84C^{1/2}$ where C is the slope (0.624) of the $1/\chi_M^{\text{corr}}$ *vs.* temperature line and was found to be 1.77 B.M. with a Weiss constant of +10°K. The molar susceptibility at any temperature in the range studied can be calculated within the range of the experimental uncertainties by inserting the given magnetic moment and slope into the above expression.

The magnetic susceptibility data for the compounds with the composition Cu(amine)(OH)(ClO_4) strongly support Pfeiffer and Glaser's[2] formulation as binuclear complexes with hydroxy bridges. The magnetic susceptibility data for μ-dihydroxy-bis-(N,N-diethyl-N′-methylethylenediamine)-dicopper(II) perchlorate which are given in Table I can be fitted to the theoretical curve calculated from the expression

$$\chi_M = \left(\frac{2g^2N\beta^2}{3kT}\right)\left(\frac{1}{1 + (1/3)\exp(J/kT)} + N\alpha\right) \qquad (1)$$

where g is the Landé splitting factor, β the Bohr magneton, N Avogadro's number, k the Boltzmann constant, J the energy separation between the singlet state and the triplet state, and $N\alpha$ the temperature independent paramagnetism of two copper(II) ions. The expression is a general one for the temperature dependence of the susceptibility of a system with a low lying singlet and a triplet state separated by an energy difference J.[9–11] The energy difference between the singlet and triplet states was calculated from the expression

$$3\exp(-J/kT_N) + 1 = J/kT_N \qquad (2)$$

and was found to be 746 × 10^{-16} erg or 1.07 kcal./mole for the N,N-diethyl-N′-methyl compound, and 815 × 10^{-16} erg or 1.17 kcal./mole for the N,N,N′,N′-tetraethyl compound. Expression 2 was derived by setting the derivative of expression 1 with respect to temperature equal to zero at the Néel temperature.

Table I

Magnetic Susceptibility Data for $[Cu_2(\text{amine})_2(OH)_2](ClO_4)_2$

T, °K.	$\chi_M^{\text{corr}} \times 10^6$, c.g.s. units	μ_{eff}, B.M.	K_{eq}
$[Cu_2\{(C_2H_5)_2NCH_2CH_2NHCH_3\}_2(OH)_2](ClO_4)_2$			
77.0	81 ± 8[a]	0	...
195.0	978 ± 2	1.19	0.203
228.8	1130 ± 15	1.39	.298
243.2	1165 ± 19	1.46	.339
274.0	1227 ± 10	1.59	.430
298.1	1271 ± 13	1.69	.515
314.2	1287 ± 5	1.75	.572
333.2	1296 ± 8	1.81	.639
353.2	1291 ± 6	1.86	.699
369.0	1284 ± 8	1.89	.738
$[Cu_2\{(C_2H_5)_2NCH_2CH_2N(C_2H_5)_2\}_2(OH)_2](ClO_4)_2$			
77.0	88 ± 23[b]	0	...
195.0	448 ± 14	0.753	0.072
231.0	626 ± 12	1.00	.135
273.8	833 ± 16	1.29	.246
297.2	881 ± 13	1.38	.292
315.7	924 ± 14	1.46	.339
332.3	933 ± 8	1.51	.372
354.2	972 ± 7	1.59	.430
369.2	976 ± 5	1.63	.463
377.7	973 ± 6	1.64	.471
383.3	973 ± 4	1.65	.478
388.2	972 ± 3	1.67	.497

[a] Diamagnetic correction is 331 × 10^{-6} c.g.s. unit. [b] Diamagnetic correction is 395 × 10^{-6} c.g.s. unit.

Equilibrium constants for the reaction

$$\text{singlet} \rightleftharpoons \text{triplet}$$

were calculated from the magnetic data. The magnetic moment at 77°K. was assumed to arise from the temperature-independent paramagnetism of the cupric ions since the first term of the Van Vleck expression added only 3 × 10^{-6} c.g.s. unit to the magnetic susceptibility at that temperature. Therefore the molar susceptibility observed at 77°K. which had been corrected for the diamagnetism of the atoms was subtracted from the molar susceptibilities observed at the other temperatures. Magnetic moments then were calculated using $\mu_{\text{eff}} = 2.84(\chi_M^{\text{corr}}T)^{1/2}$. The mole fractions of molecules in each state were calculated from the magnetic moments by assuming the singlet state to have a moment of 0.0 B.M. and the triplet state a moment of 2.90 B.M. The latter moment was estimated from $\mu_{\text{eff}} = g[S(S + 1)]^{1/2}$, for which a value for g of 2.05 was obtained from eq. 1 and the data for the N,N-diethyl-N′-methyl compound. The magnetic susceptibility data for a normal amine complex, bis-(N,N-diethylethylenediamine)-copper(II) perchlorate, also yielded a g value of 2.05. These data for the N,N-diethyl-N′-methyl and N,N,N′,N′-tetraethyl compounds are presented in Table I. A plot of log k_{eq} *vs.* $1/T$ yielded straight lines in both cases. The slopes of the lines were used to calculate ΔH^0 and ΔS^0 for each compound. The results are given in Table II.

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(9) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, Chapter 7.

(10) B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956).

(11) G. A. Barclay, C. M. Harris, B. F. Haskins, and E. Kokot, *Proc. Chem. Soc.*, 264 (1961).

TABLE II

Compound	ΔH^0, kcal./mole	ΔS^0, e.u.
$[Cu_2\{(C_2H_5)_2NCH_2CH_2NHCH_3\}_2(OH)_2](ClO_4)_2$	1.06	2.2
$[Cu_2\{(C_2H_5)_2NCH_2CH_2N(C_2H_5)_2\}_2(OH)_2](ClO_4)_2$	1.49	2.6

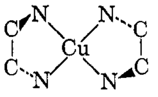
A careful examination of the temperature dependence of the infrared spectrum of bis-(N,N-diethylethylenediamine)-copper(II) perchlorate in the region 900–1250 cm.$^{-1}$ revealed that the perchlorate anion is not involved in partial covalent bonding in either the high temperature or the low temperature form. The infrared spectra were recorded at 26, 40, and 50°, and consisted of the same number of bands located at the same energies in each spectrum. The main feature of the spectra was a broad intense band at 1087 cm.$^{-1}$. This is the triply degenerate asymmetric stretching mode of the tetrahedral perchlorate anion.[12] In addition to a number of diamine bands of varying lower intensities superimposed on the asymmetric stretching band, the non-degenerate symmetric stretching vibration of ClO_4^- was present as a weak band at 931 cm.$^{-1}$. The weak absorption is in compliance with the fact that the band is theoretically forbidden in the infrared. The intensity of this band was unaffected by the crystal transformation.

The great similarity in the *d*-spacings and relative intensities in the powder patterns of bis-(N,N-diethylethylenediamine)-copper(II) and -nickel(II) perchlorates indicates that the two compounds are isomorphous.

Discussion

The Binuclear Complexes.—The singlet–triplet splitting calculated from the Néel temperature and the thermodynamic argument are in satisfactory agreement with one another and with previously reported values on similar compounds.[10] The observed entropy change of 2.2 to 2.6 e.u. is in good agreement with the value 2.2 e.u. calculated from R ln 3 where 3 is the degeneracy ratio assuming that the only contribution is that from the electronic entropy.

The Thermochromism.—The possibility that the color transition in $[Cu\{(C_2H_5)_2NC_2H_4NH_2\}_2](ClO_4)_2$ is related to an interaction between copper ions is unlikely in view of the crystal structure results.[5] In the high temperature form which is monoclinic the copper ions lie at centers of inversion at a distance of 8.5–9.5 Å. from one another. This symmetry requirement coupled with the isomorphism to the diamagnetic nickel complex strongly suggests that the *trans*-square coplanar isomer must be present in the crystal; furthermore, of the four conformers depicted below one of the centric conformers II and IV must be present.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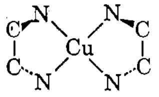
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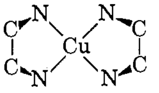
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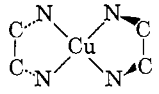
IV

The relative stabilities of conformers I and II have been discussed by Corey and Bailar,[13] who predicted that the acentric conformer I should be more stable. They did not consider III and IV. These conformers undoubtedly would be less stable for the ethylenediamine cycle, but N-substitution might alter the relative stabilities.

The structure in the low temperature triclinic crystal must be only very slightly different from the monoclinic form since the unit cell parameters change only very slightly and the relative intensities of many of the intense lines remain nearly constant. We do not know whether in the triclinic crystal the copper atoms lie at centers of inversion. The magnetic susceptibility results rule out completely the possibility of a magnetic transition, already made very unlikely in view of the crystal structure.

The band maximum of the blue form—more carefully described as deep blue-purple—occurs at 19,200 cm.$^{-1}$, 1200 cm.$^{-1}$ lower in energy than that of the red form. The seemingly drastic change in color is mainly an intensity effect, *i.e.*, no large change in ligand field is entailed. Although a lower crystal field, *i.e.*, increase in bond distances, is the common trend as the temperature is increased, it is very surprising for the intensity to increase as the crystal field decreases, especially in view of the fact that the high temperature form must be centric. However, it must be borne in mind that the crystal field actually could increase provided that a decrease in tetragonality accompanied the change; such effects have been noted in the spectra of copper(II) ammine complexes.[14]

A great number of salts of bis-(N,N-diethylethylenediamine)-copper(II) were prepared and checked for thermochromism. None of the salts with the seventeen different anions listed in the Experimental section exhibited a similar property. In order to check the effect of the size of the alkyl group substituted on the nitrogen, complexes of N,N-di-*n*-butyl- and N,N-dimethylethylenediamine were prepared. These perchlorate salts did not exhibit thermochromism. The binuclear complexes which are also undoubtedly planar did exhibit thermochromism but we have no evidence for an associated phase transformation.

There are a number of possibilities which might explain the observed crystal transition: (1) onset of free rotation of the ClO_4^- ion; (2) slight changes in positions of the ethyl groups or the ClO_4^- ions; and (3) a change in conformation in the chelate cycles.

It is not possible to make a certain choice from among these possibilities. In any case the infrared spectra rule out any tight binding between the copper ion and the perchlorate anion. Therefore, we would expect

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[12] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

[13] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[14] J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).

that any changes in the orientation of the perchlorate ion would have only a very slight effect on the crystal field at the copper ion. On the other hand, a change in the orientation of the ethyl groups or more particularly a conformational change in the ring would affect the nitrogen atoms and thus be much more effective in changing the ligand field. Such conformational changes are most likely the source of the thermochromism. The elucidation of this problem will have to wait for a complete crystal structure determination.[5]

Acknowledgment.—This research was supported by the National Science Foundation. The authors wish to thank Dr. G. Newman for the infrared measurements and Dr. C. E. Pfluger for discussions about the crystal structures.

Notes

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Formation Constants and Steric Factors in the Copper(II) Chelates of 2-Substituted Benzimidazoles

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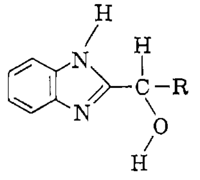
Received July 25, 1962

The acid dissociation constants and the stability constants for the Cu(II) chelates of 2-(α-hydroxyalkyl)-benzimidazoles (I) and of 2-(N-alkylaminomethyl)-benzimidazoles (II) (alkyl = H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, and n-C_5H_{11}) are presented. This preliminary study suggests that several factors are important in affecting the stability of these chelates.



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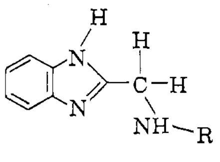

II

Experimental

Preparation of Compounds.—2-Hydroxymethyl- and 2-(α-hydroxyethyl)-benzimidazoles were prepared according to the method of Phillips.[2] Purity was established by comparing melting points and analyses with reported values[2]; m.p.: 2-hydroxymethyl-, lit. 171–172°, obsd. 170–171°; 2-(α-hydroxyethyl)-, lit. 178–179°, obsd. 180–181°.

2-(α-Hydroxypropyl)-, 2-(α-hydroxybutyl)-, and 2-(α-hydroxyamyl)-benzimidazoles have not been reported in the literature. They were successfully prepared by the method of Phillips[2] from *o*-phenylenediamine (0.02 mole) in each case and (0.03 mole) of the proper acid, namely 2-hydroxybutanoic acid, 2-hydroxypentanoic acid, and 2-hydroxyhexanoic acid, respectively. After decolorization with charcoal and three recrystallizations from 50% aqueous ethanol the white crystals obtained from each of the compounds melted at 221–222°, 181–182°, and 190–191°, respectively.

Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.2; H, 6.86; N, 15.9. Found: C, 68.1; H, 6.95; N, 15.5. *Anal.* Calcd. for $C_{11}H_{14}N_2O$: C, 69.4; H, 7.42; N, 14.7. Found: C, 69.2; H, 7.42; N, 14.5. *Anal.* Calcd. for $C_{12}H_{16}N_2O$: C, 70.6; H, 7.90; N, 13.7. Found: C, 70.5; H, 7.92; N, 13.6.

2-Aminomethylbenzimidazole was prepared by the method of Lane[3]; m.p.: lit.[3] 53°, obsd. 52–53°. The analysis agreed with theoretical values.

2-(N-Methylaminomethyl)-benzimidazole, 2-(N-ethylaminomethyl)-benzimidazole dihydrochloride, and 2-(N-butylaminomethyl)-benzimidazole were prepared according to the method of Bloom and Day[4]; m.p.: 2-(N-methylaminomethyl)-, lit.[4] 207–209° dec., obsd. 205–209° dec.; 2-(N-ethylaminomethyl)-, lit.[4] 223–225° dec., obsd. 221–225° dec.; 2-(N-butylaminomethyl)-, lit.[4] 203–204°, obsd. 204–205°. Analyses agreed with theoretical values.

2-(N-Propylaminomethyl)-benzimidazole dihydrochloride (not reported in the literature) was successfully prepared by the method of Bloom and Day[4] from propylamine (0.4 mole) and 2-chloromethylbenzimidazole (0.2 mole). The colorless prisms melted at 182–183° dec. *Anal.* Calcd. for $C_{11}H_{17}N_3Cl_2$: C, 50.4; H, 6.54; N, 16.0. Found: C, 50.4; H, 6.62; N, 16.0.

Apparatus and Procedure.—The stability constants were determined by the Bjerrum method[5] of potentiometric titration in 50% v./v. dioxane–water. The titration apparatus and procedure have been described previously.[6] Titrations were carried out using ligand to metal ratios of 8:1.

The acid dissociation constants of the ligands were determined from the titration of a mixture of ligand and acid with standard sodium hydroxide.

Calculations.—The 2-(α-hydroxyalkyl)-benzimidazoles (I) contain one weakly basic ring nitrogen and one weakly acidic —OH group. The ring nitrogen picks up a proton in acid solution to give the ion, $[HN\text{-}R\text{-}OH]^+$. The acid dissociation constants can then be defined for the two ionization processes

$$[HN\text{-}R\text{-}OH]^+ \rightleftharpoons N\text{-}R\text{-}OH + H^+;\ K_{NH^+}$$

$$N\text{-}R\text{-}OH \rightleftharpoons [N\text{-}R\text{-}O]^- + H^+;\ K_{OH}$$

The 2-(N-alkylaminomethyl)-benzimidazoles (II) contain one very weakly basic nitrogen and one relatively strongly basic nitrogen. As above, the basic nitrogens pick up protons in acid solution to give a diprotonated cation, $[HN\text{-}R\text{-}NH]^{++}$, with first and second acid dissociation constants.

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[1] (a) The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This work was also supported from research grant AM-02763-04 from the Department of Health, Education, and Welfare, Public Health Service. (b) This publication is based on a thesis submitted by H. B. Durham, in partial fulfillment of the requirements for the Ph.D. degree, to the University of Notre Dame, August, 1962. Presented at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, 1961.

[2] M. A. Phillips, *J. Chem. Soc.*, 2393 (1928).

[3] E. S. Lane, *ibid.*, 3313 (1957).

[4] A. Bloom and A. R. Day, *J. Org. Chem.*, **4**, 14 (1939).

[5] J. Bjerrum, "Metal-Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[6] H. Freiser, R. G. Charles, and W. D. Johnston, *J. Am. Chem. Soc.*, **74**, 1383 (1952).