Oxidation of 1,1-Dimethylhydrazine by Cupric Halides. The Isolation of a Complex of 1,1-Dimethyldiazene and a Salt Containing the 1,1,5,5-Tetramethylformazanium Ion

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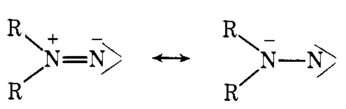
Abstract: Oxidation of 1,1-dimethylhydrazine with cupric chloride in aqueous solution at 0° produces the purple complex $[(CH_3)_2N{=}N]_2Cu_3Cl_3$. This diamagnetic complex has been characterized by elemental analysis and infrared spectroscopy. Reactions of this complex which are diagnostic for the presence of 1,1-dimethyldiazene are described. Thus the complex yields tetramethyl-2-tetrazene when treated successively with hydrochloric acid and ammonia. When a solution of $[(CH_3)_2N{=}N]Cu_3Cl_3$ in hydrochloric acid is mixed with an acidic solution of $(C_2H_5)_2N{=}NH^+$ and the mixture is made basic, it is possible to isolate the mixed tetrazene—$(C_2H_5)_2NN{=}NN(CH_3)_2$—as well as tetramethyl-2-tetrazene and tetraethyl-2-tetrazene. Oxidation of 1,1-dimethylhydrazine with cupric bromide in aqueous solution at 25° produces the salt $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$ which consists of discrete planar cations and polymeric anions. The diamagnetic salt has been characterized by elemental analysis, infrared and proton magnetic resonance spectroscopy, and by X-ray crystallography. It crystallizes in space group $P\bar{1}$ with unit cell parameters a = 9.784 (5) Å, b = 5.890 (2) Å, c = 11.615 (4) Å, α = 96.06 (2)°, β = 92.23 (4)°, γ = 100.11 (3)°, and Z = 2. The observed and calculated densities are 2.52 (1) and 2.522 g cm^{-3}, respectively. The structure was solved by direct methods; full-matrix least-squares refinement resulted in R = 0.048 for 1584 data with $F_o^2 \geq 3\sigma(F_o^2)$. Addition of ammonia to a solution of $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$ in hydrobromic acid produces $CH_3N{=}NCH{=}NN(CH_3)_2$, a previously unknown formazan. The method of formation of the cation $(CH_3)_2N_2CHN_2(CH_3)_2^+$ from 1,1-dimethylhydrazine as the sole carbon source appears to involve oxidation of the hydrazine to give 1,1-dimethyldiazene which hydrolyzes to give formaldehyde. The production of the central CH group of $(CH_3)_2N_2CHN_2(CH_3)_2^+$ from formaldehyde has been confirmed by preparation of $[(CH_3)_2N_2CDN_2(CH_3)_2][Cu_2Br_3]$ from mixtures of 1,1-dimethylhydrazine, formaldehyde-d_2, and cupric bromide.

The oxidation of 1,2-disubstituted hydrazines by cupric halides in aqueous solution has been shown to produce characteristic, red-brown, cuprous halide complexes of the corresponding 1,2-disubstituted diazenes.[2] This reaction has been utilized frequently as a means of preparation of diazenes since the diazene may be readily liberated from the complex by thermolysis or by treatment with aqueous hydroxide. These cuprous diazene complexes may also be formed by the addition of a diazene to aqueous solutions of cuprous halides. This latter reaction has been the basis of a standard test for the presence of the diazene function.

In some cases monosubstituted diazenes, which are considerably less stable than their disubstituted counterparts,[3] also form complexes with cuprous halides. Oxidation of phenylhydrazine with cupric halides in aqueous solution produces complexes of phenyldiazene.[4] The reaction of methyldiazene with cuprous chloride produces the complex $CH_3N{=}NHCuCl$;[5] however, this complex is not obtained when methylhydrazine is oxidized by cupric chloride.

The structure of one diazene complex—$CH_3N{=}NCH_3Cu_2Cl_2$—has been determined by X-ray crystallography.[6] This compound contains infinite columns of cuprous and chloride ions within which each copper is coordinated by three chloride ions. In addition each copper is coordinated by a lone pair from one nitrogen of a planar, *trans*-1,2-dimethyldiazene. Each diazene nitrogen is coordinated to a copper ion of a different column so that the diazene units form the rungs of a ladder between the cuprous-halide chains. Presumably the structures of other diazene complexes incorporate similar features, particularly the presence of polymeric cuprous halide chains and diazene coordination to copper through a nitrogen lone pair. However, the stoichiometry of these complexes apparently can vary with the identity of the components involved (*e.g.*, $(CH_3NNCH_3)Cu_2Cl_2$,[2] $(C_6H_5NNH)Cu_4Cl_4$,[4] and $CH_3NNHCuCl$[5]) and the relationship between the stoichiometry and structure has not been ascertained.

1,1-Disubstituted hydrazines, like 1,2-disubstituted hydrazines, may also undergo a two-electron oxidation. The products of this oxidation—1,1-diazenes or aminonitrenes **1**—are stable when protonated, but under neutral conditions they generally dimerize to form 2-tetrazenes **2** or tautomerize to produce hydrazones.[7] In view of the ability of a proton to stabilize the 1,1-diazenes, it appeared likely that other Lewis acids, in particular transition metal ions, might also stabilize these intermediates through coordination. The chemistry of complexes of 1,1-diazenes is of interest in two additional areas. It is possible that during nitrogen fixation a 1,1-diazene complex ($M{-}NNH_2$) is produced as an intermediate. Recent structural data on complexes containing protonated dinitrogen[8a] and a protonated azophenyl group[8b] have demonstrated the existence of M-NNRH units in two complexes. Secondly nitrenes are isoelectronic with carbenes and a large number of metal complexes of carbenoid ligands have been prepared.[9] In almost all examples of such complexes, the carbenoid carbon has been attached to a group or groups which are good π donors. Consequently, it would appear that attempts to form stable complexes of nitrenes would be most successful in the case of aminonitrenes (1,1-diazenes) where similarly a good π donor is adjacent to the potentially electron-deficient nitrene nitrogen.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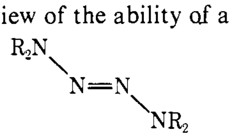
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With this background, the oxidation of 1,1-dimethylhydrazine by cupric halides has been investigated. It was anticipated that complexes of 1,1-dimethyldiazene would form and that these would have physical and structural properties which would resemble those of other cuprous diazene complexes with the important modification that the mode of diazene coordination would necessarily differ.

Experimental Section

Preparation of Compounds. $[(CH_3)_2N{=}N]_2Cu_3Cl_3$. All solutions were maintained at 0°. A solution of 21.19 g (118.8 mmol) of cupric chloride dihydrate in 90 ml of water was added to a solution of 3.57 g (4.50 ml, 59.4 mmol) of 1,1-dimethylhydrazine in 300 ml of 5% hydrochloric acid. A saturated aqueous solution of sodium acetate was added dropwise to this mixture until the pH reached 4. During this process the solution darkened and a deep purple, microcrystalline solid formed. The solid was collected by filtration, washed with water, methanol, and ether, and dried under vacuum (yield, 8.05 g). The dry product is stable for several weeks when kept under vacuum; however, storage with exposure to the atmosphere leads to rapid decomposition. One sample was pyrophoric when exposed to air. However, the nature of the product is not affected if the initial synthesis is run under anaerobic conditions; only after isolation does the solid appear to be sensitive to the atmosphere. An analogous reaction using cupric bromide yielded a dark solid whose infrared spectrum was similar to that of $[(CH_3)_2N{=}N]_2Cu_3Cl_3$; however, since this material could not be obtained in crystalline form, it was not studied further.

Anal. Calcd: C, 11.63; H, 2.93; N, 13.56; Cu, 46.14; Cl, 25.74. Found: C, 10.36; H, 2.78; N, 11.43; Cu, 46.98; Cl, 25.61.

Isolation of Tetramethyl-2-tetrazene from $[(CH_3)_2N{=}N]_2Cu_3Cl_3$. The complex $[(CH_3)_2N{=}N]_2Cu_3Cl_3$ (6.45 g, 15.6 mmol) was dissolved in 125 ml of 6 *M* hydrochloric acid at 0°. The solution was then treated with sufficient 15 *M* aqueous ammonia to increase the pH to 10. The aqueous phase was extracted with diethyl ether (12 100-ml portions). The solvent was removed on a rotary evaporator. The resulting oil was shown to be at least 98% pure tetramethyl-2-tetrazene (0.6 g, 33.3%), which was identified by comparison of its infrared and pmr spectra with those of an authentic sample.[10,11]

Isolation of Mixed 2-Tetrazenes from $[(CH_3)_2N{=}N]_2Cu_3Cl_3$. A solution of $(C_2H_5)_2N{=}NH^+$ was prepared by adding 2.22 ml (1.76 g, 20.0 mmol) of 1,1-diethylhydrazine to a slurry of 20 ml of 12 *N* hydrochloric acid and sufficient ice to give a temperature of −10° and oxidizing the hydrazine by the addition of 1.11 g (6.7 mmol) of potassium bromate dissolved in 30 ml of water at 0°. The resulting solution was rapidly mixed with a solution prepared by dissolving 4.14 g (10.0 mmol) of $[(CH_3)_2N{=}N]_2Cu_3Cl_3$ in 20 ml of 6 *M* hydrochloric acid at 0°. After mixing, the pH of the solution was rapidly adjusted to 10 by the addition of a cold solution of 15 *M* aqueous ammonia. The aqueous phase was extracted with diethyl ether (12 100-ml portions) and the solvent was removed by evaporation under vacuum. The oil (2.1 g), which remained after evaporation, was shown to consist of tetramethyl-2-tetrazene, 1,1-diethyl-4,4-dimethyl-2-tetrazene, and tetraethyl-2-tetrazene in a ratio of 1:2.4:1.4, by comparison of the pmr spectrum of this oil with pmr spectra of authentic samples of tetramethyl-2-tetrazene and tetraethyl-2-tetrazene.[11] The three tetrazenes have been separated by gas chromatography (¼ in. × 5 ft SE30 column operated at 80°) with the successive elution of tetramethyl-2-tetrazene, 1,1-diethyl-4,4-dimethyl-2-tetrazene, and tetraethyl-2-tetrazene.

$[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$. A filtered solution of 21.85 g (98.0 mmol) of cupric bromide dissolved in 75 ml of water was added to a solution of 3.75 ml (2.96 g, 49.0 mmol) of 1,1-dimethylhydrazine in 250 ml of 5% aqueous hydrobromic acid. Dropwise addition of a saturated aqueous solution of sodium acetate to the stirred reaction mixture resulted in the formation of a light tan solid which was shown to be cuprous bromide (Calcd for CuBr: Cu, 44.29. Found: Cu, 43.89.) Addition of the sodium acetate solution was continued until precipitation of a second, brown solid started. At this point, the solution was filtered and the addition of sodium acetate solution to the filtrate was continued until the pH reached 4.[12] The precipitate which formed was collected by filtration, washed with water, methanol, and ether, and dried under vacuum. The solid at this point consisted of a mixture of $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$ and cuprous bromide. The yield of the cation, $(CH_3)_2N_2CHN_2(CH_3)_2{}^+$, as determined by quantitative analysis by pmr spectroscopy using octamethyltetrasiloxane as a standard for integration, was 20% based on the utilization of 3 mol of 1,1-dimethylhydrazine in its formation. The salt was purified by dissolving it in 48% aqueous hydrobromic acid at 25°, filtering the solution, and diluting it with an equal volume of water. The solution was cooled to 0° and, after standing for several hours, the product was deposited as red-orange crystals. These crystals were collected by filtration, washed with 5% aqueous hydrobromic acid, methanol, and ether, and dried under vacuum. Crystals prepared in this way were used for the X-ray structure determination.

Anal. Calcd: C, 12.11; H, 2.64; N, 11.30; Br, 48.33. Found: C, 11.78, 10.16, 9.90; H, 2.76, 1.83, 2.73; N, 11.79, 11.46, 11.21; Br, 49.81, 49.83, 48.50.

A complex with a similar infrared spectrum could be prepared from cupric chloride and hydrochloric acid by the method outlined above. However, no method of recrystallization or purification of this material has been found.

$[(CH_3)_2N_2CDN_2(CH_3)_2][Cu_2Br_3]$. A 1.62-g (12.3 mmol) sample of methylene diacetate-d_2[13] was hydrolyzed to produce formaldehyde-d_2 by refluxing in a mixture of 0.5 ml of water and 0.05 ml of 48% hydrobromic acid for 17 hr. The solution was diluted with 25 ml of water while hot, and, after cooling, 2 *M* aqueous sodium hydroxide was added to adjust the pH to 10. 1,1-Dimethylhydrazine (0.94 ml, 0.74 g, 12.3 mmol) was added to this solution. After 5 min, a solution of 0.94 ml of 1,1-dimethylhydrazine in 125 ml of 5% aqueous hydrobromic acid was added, and then a filtered solution of 10.93 g (49.0 mmol) of cupric bromide in 40 ml of water was added. Finally, a saturated aqueous solution of sodium acetate was added dropwise with stirring to the mixture. The red-orange product formed needles with slight contamination by cuprous bromide. The product was collected by filtration, washed with water, methanol, and ether, and dried under vacuum. The pmr spectrum of the salt in acetonitrile-d_3 exhibited singlet resonances at τ 6.37 and 6.11 but no resonance due to the CH unit at 1.89. The infrared spectrum of the product was identical with that of $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$; ν_{C-D} could not be detected.

$(CH_3)_2N_2CHN_2CH_3$. A 50-g sample of unrecrystallized $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$ was dissolved in 150 ml of 25% aqueous hydrobromic acid. Aqueous ammonia (5 *M*) was added to this solution until the pH was 10. The aqueous solution was extracted with 20 50-ml portions of ether. After drying the combined ether extracts over anhydrous sodium sulfate, the ether was removed at reduced pressure on a rotary evaporator to yield 1 ml of the product as a yellow oil. Purification was effected by preparative gas chromatography on a ¼ in. by 5 ft SE-30 column operated at 90°; *m/e* 114.0899 (calcd 114.0905). On standing exposed to the atmosphere for 3 or 4 days, the compound showed alterations in its pmr and infrared spectra which indicated that it had undergone further reactions.

Physical Measurements. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Proton magnetic resonance (pmr) spectra were recorded on a Varian A-60 spectrometer. Magnetic susceptibilities were determined on a Gouy balance. Mass spectra were recorded on a Varian M66 double focusing mass spectrometer.

X-Ray Structure Determination. Preliminary precession and Weissenberg photographs (Cu Kα) suggested that the orange-red plates of $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$ were triclinic. No additional symmetry was suggested by cell reduction according to the method of Buerger.[14] Successful solution and refinement of the structure confirmed the choice of space group as $P\bar{1}$.

A crystal was chosen which had ω scan widths of less than 0.25° (peak widths at half-height) at a takeoff angle of 0.7° on a Picker FACS-1 four-circle diffractometer. The crystal had dimensions of 0.05 × 0.15 × 0.66 mm. Twelve reflections with 2θ in the range 24–38° were automatically centered on the Cu K$\bar{\alpha}$ peak (λ 1.54178 Å). A least-squares refinement of the setting angles for these reflections gave unit cell parameters at 19 ± 2° of a = 9.784 (5) Å, b = 5.890 (2) Å, c = 11.615 (4) Å, α = 96.06 (2)°, β = 92.23 (4)°, and γ = 100.11 (3)°. All results and discussions are based on this triclinic cell. The right-handed reduced cell has parameters of a = 5.89 Å, b = 9.78 Å, c = 11.61 Å, α = 92.23°, β = 96.06°, and γ = 100.11°. This reduced cell is related to the working cell by $a_r = -b$, $b_r = -a$, and $c_r = -c$. The density of the crystal was measured by the gradient column technique, using mixed solutions of bromomethane–carbon tetrachloride and 1,1,2,2-tetrabromomethane–bromomethane, and was found to be 2.52(1) g cm^{-3}. The calculated density, assuming two formula weights per unit cell, is 2.522 g cm^{-3}.

An incident beam monochromator equipped with a graphite crystal was used to obtain Cu Kα radiation. The θ–2θ axis of the monochromator was perpendicular to the θ-2θ axis of the diffractometer. Data were collected using the θ-2θ scan technique and a scan range from $2\theta_{\mathrm{CuK}\alpha_1} - 1.1°$ to $2\theta_{\mathrm{CuK}\alpha_2} + 1.1°$ at a takeoff angle of 2.7°. The scan rate was 1°/min and background measurements of 10 sec were taken at each end of the scan. The pulse height analyzer was set to admit ~90% of the Cu Kα peak and the scintillation counter was 24 cm from the crystal. Copper foils with attenuation factors of 2.2 were inserted into the diffracted beam whenever the count rate exceeded 10^3 counts sec^{-1}. During data collection the intensities of three reflections were monitored every 50 reflections. There was no systematic change in the intensities of the three standards. The maximum standard deviation of any standard from its mean value was 0.73%. An equipment failure during data collection required two separate scale factors for the data set.

A total of 1982 reflections were collected with $2\theta \leq 115°$. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.[15,16] The program used was UAFACS2, a greatly modified version of Raymond's UCFACS.[17] The polarization correction used was

$$P = 0.5(\cos^2 2\theta_{\mathrm{m}} + \cos^2 2\theta)$$

where θ_{m} is the Bragg angle of the monochromator and θ is the Bragg angle of the observed reflection. Standard deviations were assigned to the intensities by the formula

$$\sigma(F^2) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pF^2)^2]^{1/2}$$

where CT is the total integrated peak height obtained in time t_c and B_1 and B_2 are the background counts each obtained in time t_b; F^2 is the corrected intensity and p was taken as 0.04.

The absorption coefficient for the compound for Cu Kα radiation is 164.26 cm^{-1}. The faces of the crystal were identified as $\{101\}$, $\{010\}$, $\{001\}$, and $(\bar{1}\bar{1}\bar{1})$, and the crystal was carefully measured. Sample calculations showed that the absorption correction ranged from 2.24 to 11.1 and the data were corrected for absorption by the analytical method.

Solution and Refinement of Structure. A three-dimensional Patterson function computed from the intensity data proved quite difficult to interpret. Therefore, after the calculation of normalized structure factors, the phases of the 263 reflections with $E \geq 1.5$ were calculated using the MULTAN group of direct methods programs. The two resulting phase sets with the highest figures of merit were used to calculate E-maps. However, the heavy atom positions determined from these maps did not reproduce the Patterson map vectors. Close examination of the data showed that 219 of the 1982 data gathered were not crystallographically unique; one of the nonunique reflections was included in the starting set for phase assignment. After the duplicate data were eliminated phases were calculated for 230 reflections with $E \geq 1.37$. The phase set with the highest figure of merit, 1.017, was used to calculate an E-map which revealed all the heavy atoms in positions consistent with the Patterson map. Two cycles of least-squares refinement of these positions with a single isotropic thermal parameter gave

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o = 0.352$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{1/2} = 0.464$$

All least-squares refinements were based on F_o, with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. The weights w were taken as $4F_o{}^2/\sigma^2(F_o)^2$. The atomic scattering factors for C, N, and O were from the usual tabulations.[19] Those for Cu and Br were from Cromer and Waber.[20]

A difference electron-density map revealed the positions of nine non-hydrogen atoms, which were refined with individual isotropic thermal parameters to $R_1 = 0.142$ and $R_2 = 0.190$. From the coordinates of these atoms it was apparent that they consisted of two $(CH_3)_2N_2$ groups which were well separated from the Cu and Br atoms but bonded to a central atom of low electron density. From the chemical analysis this central atom could only be C or O.

Two separate refinements with all atoms assigned individual anisotropic thermal parameters were performed after correction of the data for absorption. In the first refinement the central atom was assumed to be oxygen and in the second, carbon. After two cycles of refinement, the model containing oxygen converged to $R_1 = 0.052$ and $R_2 = 0.082$, while the model with carbon gave $R_1 = 0.050$ and $R_2 = 0.079$. Using the tables prepared by Hamilton,[21] the model with carbon can be shown to be better than the oxygen model at the 0.05 level of significance. A difference electron-density map based on the oxygen model showed the central atom position in a hole of negative electron density, whose shape indicated that the atom had larger thermal parameters than adjacent atoms. There is no such hole in the difference map for the other model; the position of the carbon atom has a positive electron density of less than 0.1 eÅ^{-3}. On this map, which contained no peaks higher than 0.726 eÅ^{-3}, the positions of several hydrogen atoms could be determined. Peak heights ranged from 0.726 to 0.481 eÅ^{-3}. A hydrogen bonded to the middle carbon was clearly visible. The conclusion from the X-ray data that the compound contained the $[(CH_3)_2N_2CHN_2(CH_3)_2]^+$ cation was verified by the experiments with formaldehyde-d_2 (*vide supra*).

The final refinement, with the effects of anomalous dispersion included in F_c,[22] converged to $R_1 = 0.048$ and $R_2 = 0.073$ after two cycles for 1584 data with $F_o{}^2 \geq 3\sigma(F_o)^2$. The values of $\Delta f'$ and $\Delta f''$ calculated by Cromer were used for Cu and Br.[23] Since most intense low-order reflections had $F_o \geq F_c$, no extinction correction was made. An analysis of the weighting scheme showed that $w|\Delta F|^2$ was not a function of the indices, $|F_o|$, or $\sin\theta/\lambda$. The standard deviation of a reflection of unit weight is 3.427. Final structure parameters appear in Table III. A list of $10|F_o|$ and $10|F_c|$ is available.[24]

Results and Discussion

Preparation and Characterization of $[(CH_3)_2N{=}N]_2Cu_3Cl_3$. The oxidation of 1,1-dimethylhydrazine by cupric halides in aqueous solution produces two different types of products. The product obtained depends on the temperature and the stability of the product is dependent on the anion (chloride or bromide) present. Treatment of 1,1-dimethylhydrazine with cupric chloride in hydrochloric acid at 0° followed by a gradual increasing of the pH produces a microcrystalline, purple solid. Unfortunately no method has been found which allows any further purification of this material. However, this compound appears to be homogeneous under a microscope, and the data outlined below are consistent with the formulation $[(CH_3)_2N{=}N]_2Cu_3Cl_3$, **3**, and with the presence of 1,1-dimethyldiazene rather than its dimer tetramethyl-2-tetrazene. Reproducible microanalytic data have been difficult to obtain for this complex as well as for the more readily characterized $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$ (*vide infra*). The data presented in the experimental section refer to a freshly prepared specimen which underwent minimal contact with the atmosphere after isolation. These data along with the observation that the compound is diamagnetic suggest that copper is present in the complex as Cu(I). The infrared spectrum (Table I) of **3** exhibits no absorption in the region above 3050 cm^{-1} where a N-H stretch might occur. Since monosubstituted diazene-cuprous halide complexes[4a,5] and cuprous halide complexes of hydrazines[4a] display strong N-H stretching vibrations, it is apparent that no N-H units are present in **3**. The infrared spectrum does contain two bands in the region 1550-1630 cm^{-1}, which may be $\nu_{\mathrm{N=N}}$.

The strongest evidence for the presence of 1,1-dimethyldiazene in **3** comes from the chemical reactions of this material. Like other cuprous halide diazene complexes, **3** dissolves only in solvents which can effectively coordinate Cu(I). When complex **3** is dissolved in hydrochloric acid and then this solution is made basic through the addition of aqueous ammonia, it is possible to extract tetramethyl-2-tetrazene from the aqueous phase. The isolation of the tetrazene in this manner is in itself good evidence that tetramethyl-2-tetrazene was not present in the complex **3**. This paradoxical situation arises because tetramethyl-2-tetrazene is unstable under acidic conditions which cause its decomposition to a variety of products.[25,26] Consequently if

Table I. Infrared Spectral Data

Compound	ν (cm^{-1})
$[(CH_3)_2N{=}N]_2(CuCl)_3$[a]	2945 sh, 2915 m, 2850 vw, 1624 m, 1555 s, 1431 w, 1382 s, 1155 m, 980 w, 730 m
$[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$[a]	3020 vw, 1554 w, 1501 s, 1465 s, 1401 m, 1379 s, 1256 s, 1114 m, 1047 w, 975 w, 835 w, 807 w, 720 w
$[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Cl_3]$[a]	2940 vw, 1505 s, 1463 w, 1401 m, 1370 w, 1334 m, 1022 w, 902 w, 802 w, 743 m
$(CH_3)_2N_2CHN_2CH_3$[b]	2955 m, 2905 s, 2866 m,sh, 2796 w, 1629 m, 1560 s, 1474 s, 1425 m, 1349 m, 1299 m, 1185 m, 1083 vs, 987 m, 839 m, 685 w
$(CH_3)_2N_4(CH_3)_2$[b]	3001 w, 2959 s, 2857 s, 2821 m, 2787 w, 1464 s, 1436 sh, 1275 s, 1240 m, 1140 m, 1036 w, 1000 vs, 822 m

[a] Nujol and fluorocarbon mulls. [b] Neat film.

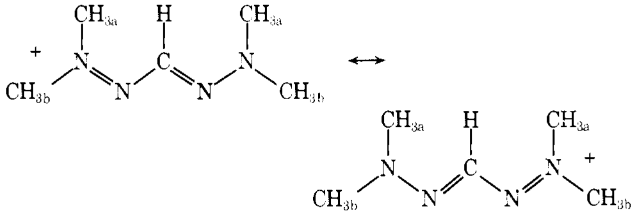
tetramethyl-2-tetrazene were present in **3**, treatment of the complex with hydrochloric acid would have been expected to produce the decomposition products of the tetrazene–methylamine, dimethylamine, formaldehyde, and tetramethylhydrazine. However, none of these were obtained after acid treatment of **3**.

Further evidence of the existence of 1,1-dimethyldiazene in **3** comes from a variant of the cross coupling experiment performed by McBride and Kruse.[10] These workers showed that when acidic, aqueous solutions of 1,1-dimethylhydrazine and 1,1-diethylhydrazine were separately oxidized by potassium bromate and then combined, made basic through the addition of hydroxide, and extracted with ether, it was possible to isolate the three tetrazenes—tetramethyl-2-tetrazene, 1,1-diethyl-4,4-dimethyl-2-tetrazene, and tetraethyl-2-tetrazene.The isolation of the mixed tetrazene, 1,1-diethyl-4,4-dimethyltetrazene, is strong evidence for the presence of 1,1-disubstituted diazenes as acid stable intermediates in the oxidation of the corresponding hydrazines, since McBride and Kruse were able to show that mixtures of tetramethyl-2-tetrazene and tetraethyl-2-tetrazene did not exchange substituents under the conditions of the cross coupling experiment. Similarly we find that addition of a cold, acidic solution of 1,1-diethyldiazenium ion, $(CH_3CH_2)_2N{=}NH^+$ (prepared by the oxidation of 1,1-diethylhydrazine by potassium bromate), to a cold, acidic solution of the copper complex **3** followed by treatment with base and extraction with ether yields the three tetrazenes—tetramethyl-2-tetrazene, 1,1-diethyl-4,4-dimethyl-2-tetrazene, and tetraethyl-2-tetrazene in nearly statistical distribution.

From these experiments we conclude that the complex **3** contains a precursor of tetramethyl-2-tetrazene and not the tetrazene itself. Both the infrared spectrum and the color of the complex (cuprous–hydrazine complexes are white) indicate that the precursor is not 1,1-dimethylhydrazine. Consequently the presence of 1,1-dimethyldiazene in **3** is the only reasonable explanation of the properties of this material. It appears then that 1,1-dimethyldiazene can be stabilized by some degree through coordination to copper. Judging from its solubility properties, $[(CH_3)_2N{=}N]_2Cu_3Cl_3$ probably contains some type of polymeric CuCl network. It is also likely that nitrogen-2 of 1,1-dimethyldiazene is coordinated by one or two cuprous ions in this solid. Unfortunately, however, the physical properties of the complex have not allowed a more extensive investigation of its structure.

Preparation and Characterization of $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$. Oxidation of 1,1-dimethylhydrazine with cupric chloride or cupric bromide in aqueous solution at 25° produces orange-red solids which are definitely not identical with the diazene complex **3**. The complex $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$ (**4**) obtained from oxidation with cupric bromide has been well characterized since it may be purified by recrystallization. The product obtained by oxidation with cupric chloride could not be purified and extensive characterization has not been carried out on this species. Because the infrared spectra of the products obtained from cupric bromide and chloride are similar, we believe that the chloride product is $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Cl_3]$ with cuprous chloride present as an impurity.

The preparation of **4** proceeds as follows. Addition of a saturated aqueous solution of sodium acetate to a solution of 1,1-dimethylhydrazine and cupric bromide in 5% aqueous hydrobromic acid initially produces a light tan precipitate which has been identified as cuprous bromide by its copper content and its lack of detectable infrared absorption in the region 4000–650 cm^{-1}. Further addition of aqueous sodium acetate causes the precipitation of the orange-red product **4**. This material may be recrystallized from 48% hydrobromic acid to yield beautiful orange-red needles. Although this material exhibits many properties which are similar to those of cuprous diazene complexes—particularly its color and lack of solubility in solvents which cannot coordinate cuprous ion—it is not a diazene complex but a salt which contains the discrete, resonance stabilized 1,1,5,5-tetramethylformazanium ion **5** and a polymeric anion with the composition $Cu_2Br_3^-$. The spectroscopic and chemical data outlined below in conjunction with the X-ray crystallographic results establish the structure.



5

The formulation of the salt **4** as a compound containing Cu(I) is based on the following observations. A magnetic susceptibility determination on the solid indicates that it is diamagnetic. No electron spin resonance (esr) absorptions could be detected in samples of the solid at 77° or 298°K or in solutions of **4** in acetonitrile.

The complex is sufficiently soluble in acetonitrile to allow observation of the pmr spectrum (Table II) of the cation. This spectrum shows no line broadening which would be expected if any cupric copper were present. The pmr spectrum of the cation consists of three singlets at τ 6.37, 6.11, and 1.89 with the intensity ratio 6:6:1. The methyl resonances occur as two distinct absorptions because the ion is constrained to planarity by multiple bonding within the N_2CN_2

Table II. Proton Magnetic Resonance Spectral Data

Compound	Chemical shifts (τ), relative intensities, and coupling constants (Hz)
$(CH_3)_2NN{=}NN(CH_3)_2$[a]	7.20
$(CH_3)_2NN{=}NN(CH_2CH_3)_2$[a]	7.22 (3 H), 8.88 (3 H, J_{HH} = 7.1), 6.71 (2 H, J_{HH} = 7.2)
$(CH_3CH_2)_2NN{=}NN(CH_2CH_3)_2$[a]	8.88 (3 H, J_{HH} = 7.1), 6.74 (2 H, J_{HH} = 7.2)
$CH_3N{=}NCH{=}NN(CH_3)_2$[b]	6.86 (6 H), 6.15 (3 H), 2.23 (1 H)
$[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$[c]	6.37 (6 H), 6.11 (6 H), 1.89 (1 H)

[a] In chloroform-d_1 solution. [b] In carbon tetrachloride solution. [c] In acetonitrile-d_3 solution.

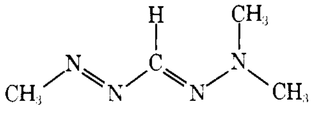
Table III. Final Atomic Parameters for $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$

Atom	x	y	z	$10^3\beta_{11}$	$10^3\beta_{22}$	$10^3\beta_{33}$	$10^3\beta_{12}$	$10^3\beta_{13}$	$10^3\beta_{23}$
Br_1	0.3764 (1)	0.1941 (1)	−0.0745 (1)	8.3 (1)	20.9 (3)	6.8 (1)	2.2 (2)	0.5 (1)	1.7 (1)
Br_2	−0.2119 (1)	0.3165 (1)	−0.1115 (1)	8.2 (1)	20.0 (3)	9.9 (1)	4.0 (2)	1.1 (1)	3.0 (1)
Br_3	0.4623 (1)	0.3063 (1)	0.2791 (1)	11.5 (1)	21.8 (4)	7.9 (1)	3.1 (2)	0.0 (1)	3.0 (1)
Cu_1	0.4112 (1)	0.0036 (2)	0.1130 (1)	14.2 (2)	31.2 (6)	11.7 (1)	1.3 (3)	0.6 (1)	1.2 (2)
Cu_2	0.4125 (1)	0.4965 (3)	0.1126 (1)	13.7 (2)	36.3 (6)	12.2 (1)	8.9 (3)	0.3 (1)	5.7 (2)
N_1	0.240 (1)	0.027 (1)	−0.495 (1)	10 (1)	30 (2)	8 (1)	5 (1)	0 (1)	4 (1)
N_2	0.162 (1)	0.158 (1)	0.471 (1)	9 (1)	25 (3)	10 (1)	4 (1)	2 (1)	2 (1)
N_3	0.021 (1)	0.274 (1)	0.346 (1)	7 (1)	24 (3)	10 (1)	6 (1)	2 (1)	2 (1)
N_4	−0.037 (1)	0.268 (1)	0.242 (1)	9 (1)	18 (2)	10 (1)	4 (1)	1 (1)	3 (1)
C_1	−0.265 (1)	0.186 (2)	−0.434 (1)	19 (1)	28 (4)	10 (1)	12 (2)	0 (1)	−3 (1)
C_2	0.311 (1)	0.090 (2)	−0.378 (1)	16 (1)	40 (5)	9 (1)	6 (2)	−4 (1)	−2 (2)
C_3	0.106 (1)	0.118 (1)	0.361 (1)	7 (1)	25 (3)	9 (1)	1 (1)	0 (1)	3 (1)
C_4	−0.130 (1)	0.436 (2)	0.230 (1)	13 (1)	33 (4)	15 (1)	13 (2)	1 (1)	3 (2)
C_5	−0.008 (1)	0.124 (2)	0.139 (1)	12 (1)	25 (3)	9 (1)	6 (1)	0 (1)	0 (1)

framework. Consequently the methyl groups a and b in **5** occur in distinguishable environments. Similar effects due to restricted rotation about C–N multiple bonds have been observed in the closely related amidinium ions.[27] The chemical shifts of the various protons in **5** are similar to those observed for amidinium ions.[27]

Neither the pmr spectrum nor the infrared spectrum of **4** shows any evidence for the presence of N–H functions in **4**. The infrared spectrum of **4** in the region 4000-650 cm^{-1} consists entirely of absorptions which may be ascribed to the cation **5**. The occurrence of absorptions in the 1600-1450-cm^{-1} region of the spectrum is in accord with the presence of a multiply bound N_2CN_2 framework.

Further evidence for the presence of the cation **5** in the salt **4** comes from the isolation of 1,5,5-trimethylformazan (**6**), which may be recovered in low yield after treatment of **4** with hydrobromic acid and ammonia. The new formazan **6** has been characterized by high resolution mass spectroscopy and by its pmr spectrum which consists of resonances at τ 6.86 (6 H, $N(CH_3)_2$), 6.15 (3 H, NCH_3), and 2.23 (1 H, C–H) (carbon tetrachloride solution). In addition the infrared spectrum of **6** is also consistent with this structure; in particular no N–H stretching vibrations are observed.



6

Description of the Structure of $[(CH_3)_2N_2CH-N_2(CH_3)_2][Cu_2Br_3]$. The ionic compound consists of polymeric $(Cu_2Br_3)_n^{n-}$ anions and monomeric $[(CH_3)_2N_2CHN_2(CH_3)_2]^+$ cations. Figure 1 shows the numbering scheme of the cation and the relative thermal motions of the atoms. A labeled perspective view of the anion, showing the coordination around all the Cu atoms, is given in Figure 2. Table III gives the final atomic parameters and Table IV gives a list of interatomic distances and angles. The estimated standard deviations of the distances were derived from the variance-covariance matrix from the final cycle of least-squares refinement.

The polymeric anion chain, which runs up the b axis of the unit cell, can best be described as a ladder of Cu atoms, each tetrahedrally coordinated by Br atoms. Its structure is the same as that reported by Rømming and Waerstand for the anion in benzenediazonium tribromodicuprate(I).[28]

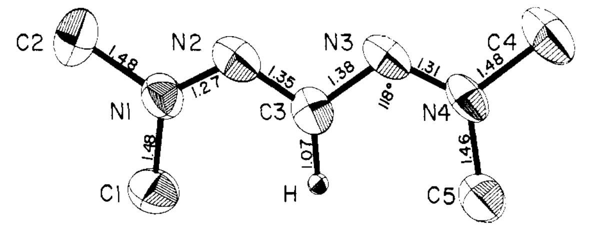


Figure 1. Numbering scheme and view of the $[(CH_3)_2N_2CHN_2(CH_3)_2]^+$ cation.

Table IV. Interatomic Distances and Angles for $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$

Atoms	Distance (Å)	Atoms	Angle (deg)
Cu_1–Cu_1'	3.224 (3)	Cu_1–Br_1–Cu_1'	76.45 (6)
Cu_2–Cu_2'	3.201 (3)	Cu_2–Br_1–Cu_2'	76.22 (6)
Cu_1–Cu_2	2.904 (2)	Cu_1–Br_1–Cu_2	67.66 (5)
Cu_1'–Cu_2'	2.991 (2)	Cu_1'–Br_1–Cu_2'	70.51 (6)
Br_1–Cu_1	2.609 (2)	Cu_1–Br_1–Cu_2'	114.04 (6)
Br_1–Cu_1'	2.602 (2)	Cu_1'–Br_1–Cu_2	113.92 (6)
Br_1–Cu_2	2.607 (2)	Cu_1'–Br_2–Cu_2'	75.78 (6)
Br_1–Cu_2'	2.580 (2)	Cu_1–Br_3–Cu_2	73.40 (6)
Br_2–Cu_1'	2.442 (2)	Br_1–Cu_1–Br_1'	103.55 (6)
Br_2–Cu_2'	2.427 (2)	Br_1–Cu_1–Br_2'	106.64 (7)
Br_3–Cu_1	2.431 (2)	Br_1–Cu_1–Br_3	109.21 (6)
Br_3–Cu_2	2.428 (2)	Br_2'–Cu_1–Br_3	119.40 (7)
C_1–N_1	1.48 (1)	Br_1–Cu_1–Br_2'	105.39 (7)
C_2–N_1	1.48 (1)	Br_1–Cu_1–Br_3'	111.41 (7)
C_4–N_4	1.48 (1)	Br_1–Cu_2–Br_1'	103.78 (6)
C_5–N_4	1.46 (1)	Br_1–Cu_2–Br_2'	106.06 (7)
N_1–N_2	1.27 (1)	Br_1–Cu_2–Br_3	109.40 (6)
N_3–N_4	1.31 (1)	Br_1'–Cu_2–Br_2'	106.50 (6)
N_2–C_3	1.35 (1)	Br_1'–Cu_2–Br_3	111.49 (7)
N_3–C_3	1.38 (1)	Br_2'–Cu_2–Br_3	118.52 (7)
C_3–H	1.07	C_1–N_1–C_2	117.6 (7)
		C_1–N_1–N_2	124.7 (7)
		C_2–N_1–N_2	117.7 (8)
		N_1–N_2–C_3	119.1 (7)
		N_2–C_3–N_3	109.0 (7)
		C_3–N_3–N_4	117.6 (7)
		N_3–N_4–C_5	124.7 (6)
		C_4–N_4–C_5	119.2 (7)

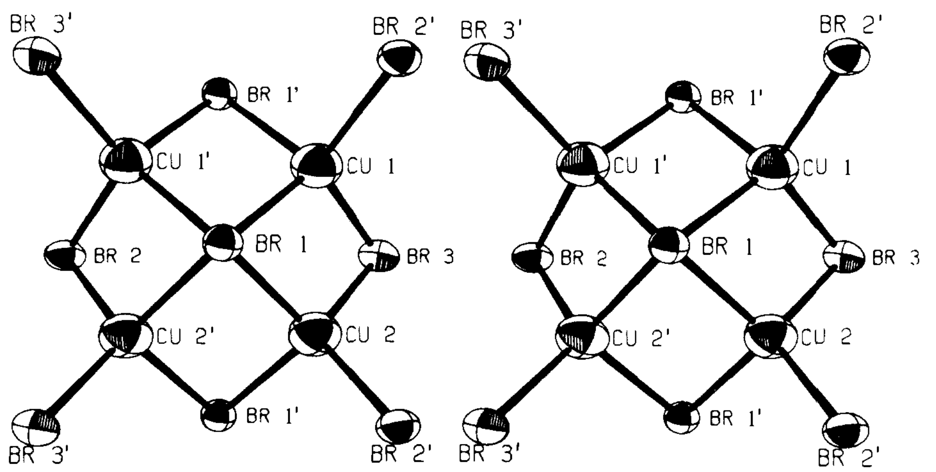


Figure 2. Stereoview of a segment of the $[Cu_2Br_3]_n^{n-}$ anion, showing coordination around the Cu(I) ions.

Two of the bromines, Br_2 and Br_3, bridge two Cu atoms with an average Cu ··· Br distance, 2.432 (2) Å, slightly shorter than that found in CuBr.[29] Since Br_1 coordinates to four copper atoms, the average Cu ··· Br_1 distance is, as expected, somewhat longer, 2.600 (2) Å. Similar Cu ··· Br distances of 2.46 and 2.59 Å are found in the polymeric $CuBr \cdot CH_3CN$ complex, although in this case both Br atoms appear to be chemically equivalent.[30]

Crystallographic inversion centers lie between the pairs of Cu atoms. The average distance between these atoms, 3.213 (3) Å, is greater than that between the consecutive Cu atoms in the chain, 2.948 (2) Å, which are linked by bridging two-coordinate bromines, in addition to the four-coordinate Br_1. The angles at the former bromine atoms, 75.78 (6) and 73.40 (6)°, are smaller than most reported M–Br–M angles, but an angle as acute as 63.9 (2)° has been reported for an iodine bridging atom.[31]

No symmetry is imposed on the cation crystallographically, but the five central non-hydrogen atoms lie nearly in a plane. The equation of the weighted least-squares plane through these atoms is $6.74x + 3.18y + 4.27z - 3.82 = 0$ (triclinic coordinates). Distances from this plane are shown in Table V. Further evidence for the delocalized electron system suggested by the planarity is given by the bond lengths and angles. The average N ··· N distance, 1.29 (1) Å, is greater than the N ··· N double bond distance in 1,2-dimethyldiazene, 1.254 Å,[32] but considerably shorter than the N ··· N single bond distance in 1,1-dimethylhydrazine, 1.45 (3) Å.[33] All the angles around the nitrogen atoms are within 5° of 120°, the idealized bond angle for atoms with sp^2 hybridization. The average C_3 ··· N distance, 1.37 (1) Å, is slightly greater than the partial double C ··· N bonds in the methylguanidinium ion 1.33 Å,[34] or formamide, 1.34 (7)Å,[35] and very similar to the aromatic C ··· N bond in pyrrole, 1.383 Å.[36]

The hydrogen atom shown in Figure 1 was clearly visible in the final difference electron density map, but its position was not refined. This difference map showed no peaks near any nitrogen atoms, in agreement with the infrared spectrum. Several possible methyl hydrogens were also visible on the map but have not been included in the figure.

Table V. Distances of the Five Central Atoms of the Cation from the Least-Squares Plane $6.74x + 3.18y - 4.27z - 3.82 = 0$ (triclinic coordinates) in $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$

Atoms	Distance (Å)	Atoms	Distance (Å)
N_1	−0.009 (7)	N_4	0.011 (6)
N_2	0.023 (7)	C_3	−0.007 (7)
N_3	0.022 (6)		

The methyl groups of the cation lie close to the plane of the five central atoms. The equation of a weighted least-squares plane through the entire cation is $6.78x + 3.18y - 4.14z - 3.76 = 0$ (triclinic coordinates). Distances from this plane are shown in Table VI. The slight tipping of the methyl groups out of this plane probably facilitates packing in the crystal. The C_4–N_4–C_5 plane is twisted in the opposite direction from the C_1–N_1–C_2 plane, with a dihedral angle of 16.1 (6)° between the planes.

As can be seen in Figure 3, the cations pack in pairs about inversion centers. Stacks of these pairs lie between the anion chains which run along the *b* axis of the unit cell. There are several contacts between the methyl carbons and the bromine atoms that are less than the sum of their van der Waal's radii, 3.95 Å.[37] The closest contact is 3.518 Å between Br_1 and C_2. The closest contact between cations is 3.423 Å between C_5 atoms in adjacent double stacks. The hydrogen atoms of these methyl carbons are required to have a staggered configuration by the inversion center. The distance between successive pairs of cations in each stack is the length of the *b* axis, 5.890 (2) Å.

The Mechanism of Formation of $[(CH_3)_2N_2CHN_2(CH_3)_2]^+$. The cation **5** has never previously been reported and its mode of formation requires explanation. Of particular interest is the origin of the central C–H unit. Since the cation may be prepared under conditions in which 1,1-dimethylhydrazine is the only carbon containing species, this C–H unit must be derived from the hydrazine. The sequence of reactions 1–5 offers a reasonable route for the formation of **5.** The initial step is expected in view of the well-documented ability of cupric ion to oxidize other hydrazines and the isolation of **3.** Step 2, the tautomerism and subsequent hydrolysis of the diazenium ion to produce formaldehyde, has been established previously in experiments which have detected formaldehyde subsequent to the oxidation of 1,1-dimethylhydrazine in aqueous solution.[38] Formaldehyde has also been implicated in the formation of 1,4-dihydro-*s*-tetrazine which occurs during the oxidation of 1,1-dimethylhydrazine by iodate ion in sulfuric acid.[39] The third reaction is also well established; formaldehyde di-

Table VI. Distances of Cationic Atoms from the Least-Squares Plane $6.78x + 3.18y - 4.14z - 3.76 = 0$ (triclinic coordinates) in $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$

Atoms	Distance (Å)	Atoms	Distance (A)
N_1	0.001 (7)	C_1	−0.210 (12)
N_2	0.025 (7)	C_2	0.197 (12)
N_3	−0.043 (6)	C_3	−0.021 (7)
N_4	0.026 (6)	C_4	−0.075 (11)
		C_5	0.144 (9)

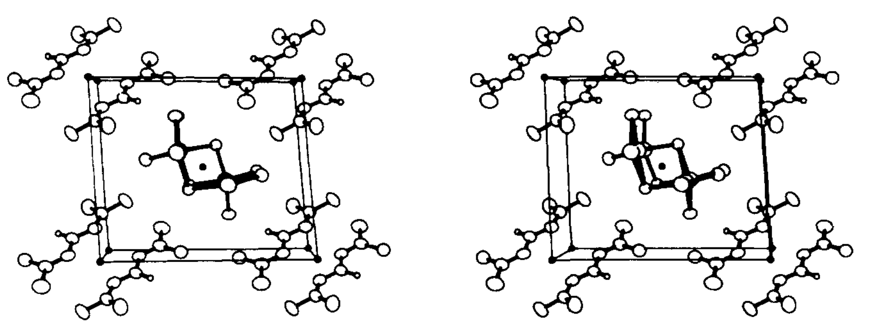
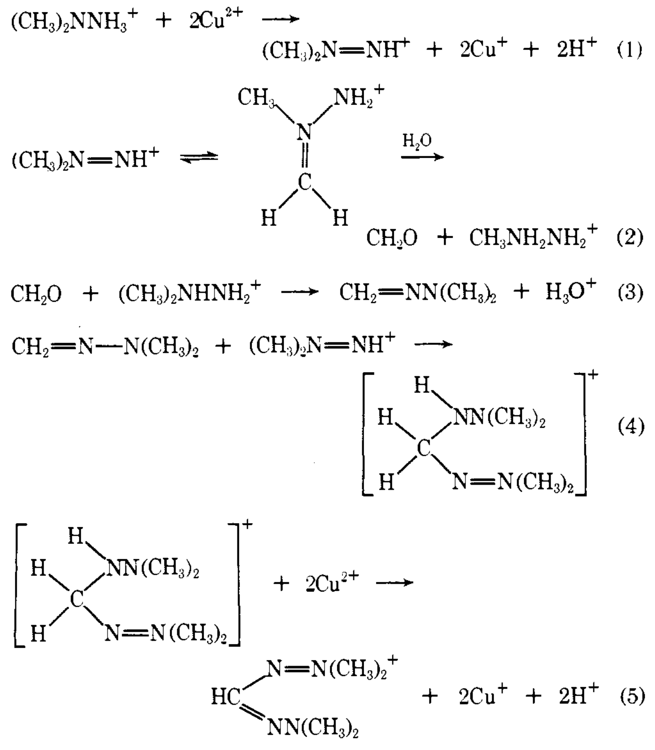


Figure 3. Stereoview of crystal packing in $[(CH_3)_2N_2CHN_2(CH_3)_2][Cu_2Br_3]$, looking down the *b* crystal axis, with the *a* axis vertical. Inversion centers are shown as small black circles.



$$\mathrm{(CH_3)_2NNH_3^+ + 2Cu^{2+} \longrightarrow (CH_3)_2N{=}NH^+ + 2Cu^+ + 2H^+} \quad (1)$$

$$\mathrm{(CH_3)_2N{=}NH^+ \rightleftharpoons CH_3(NH_2^+)N{=}CH_2 \xrightarrow{H_2O} CH_2O + CH_3NH_2NH_2^+} \quad (2)$$

$$\mathrm{CH_2O + (CH_3)_2NHNH_2^+ \longrightarrow CH_2{=}NN(CH_3)_2 + H_3O^+} \quad (3)$$

$$\mathrm{CH_2{=}N{-}N(CH_3)_2 + (CH_3)_2N{=}NH^+ \longrightarrow [H_2C(NHN(CH_3)_2)(N{=}N(CH_3)_2)]^+} \quad (4)$$

$$\mathrm{[H_2C(NHN(CH_3)_2)(N{=}N(CH_3)_2)]^+ + 2Cu^{2+} \longrightarrow HC(N{=}N(CH_3)_2^+)({=}NN(CH_3)_2) + 2Cu^+ + 2H^+} \quad (5)$$

methylhydrazone has been previously isolated from this reaction.[40] The addition of the diazenium ion to a hydrazone (step 4) has been previously postulated to account for other reactions of the 1,1-diazenium ion.[41] Additionally this reaction also resembles the electrophilic addition of a diazonium ion to a hydrazone, a reaction which has been utilized in the preparation of formazans.[42,43] The final step, the oxidative dehydrogenation to form a CN double bond, has precedent in a number of copper ion oxidations.[44]

Several observations made during the formation of **4** are also in agreement with this scheme. Since the oxidation of 1,1-dimethylhydrazine to 1,1-dimethyldiazene involves the loss of two protons, the extent and rate of hydrazine oxidation has been controlled by starting with acidic conditions and gradually raising the pH. Under these conditions excess 1,1-dimethylhydrazine will be present as 1,1-dimethyldiazene is formed, as is required by the reaction scheme. The initial precipitation of cuprous bromide is consistent with utilization of some cupric ion to generate the diazenium ion. However, during the early stage of the reaction, the succeeding reactions 2–5 do not proceed with sufficient rapidity to generate a sufficient quantity of the cation **5** to have its salt precipitate. Additionally the overall stoichiometry requires that at least six cuprous ions are present for each cation **5** that is formed, so that cuprous ion in addition to that necessary to form the salt $C_5H_{13}N_4Cu_2Br_3$ will always be present. However, if formaldehyde is added to the system prior to the cupric ion oxidation, then the initial precipitation of cuprous bromide is nearly eliminated presumably because reaction 2 is no longer necessary. Step 3 may proceed immediately and the quantity of cuprous bromide produced is reduced. If formaldehyde-d_2 is introduced into the system prior to oxidation by cupric ion, then the cation **5** is labeled with deuterium at the central carbon atom. This further supports the argument that this crucial fragment originates from formaldehyde.

It is clear that copper plays several roles in the formation of the cation **5**. Cupric ion is responsible for carrying out two distinct oxidations (eq 1 and 5). The reaction scheme has been written using two-electron oxidation steps. Radical intermediates are almost certainly involved in these oxidations since individual cupric ions are one-electron oxidants, and it is possible that a radical coupling step may replace reaction **4** in the detailed mechanism. Cuprous ion is, of course, involved in the lattice of the salt **4**, and the availability of a suitable counterion that enables the formation of a stable lattice is critical for the isolation of the cation. Additionally copper ions may also play a role in activating or organizing some of the reacting species in the various steps, but no evidence is available at present on this possible function.

1,5,5-Trimethylformazan (**6**) is also a new compound. All previous preparations of formazans that we are aware of[42,43] have required that at least one of the two terminal nitrogens bear an aromatic substituent. Consequently **6** represents the simplest formazan prepared to date. Although the present synthesis of **6** does not offer a general route to new formazans, it may be possible to devise a new method of formazan synthesis based on reactions 3–5.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-75-501.

References and Notes

(1) (a) University of California, (b) University of Arizona.
(2) O. Diels and W. Koll, *Justus Liebigs Ann. Chem.*, **443**, 262 (1925).
(3) E. M. Kosower, *Accounts Chem. Res.*, **4**, 193 (1971).
(4) (a) D. Petredis, A. Burke, and A. L. Balch, *J. Amer. Chem. Soc.*, **92**, 428 (1970); (b) H. H. Szmant and A. J. Mata, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14–18, 1970.
(5) M. N. Ackermann, *Inorg. Chem.*, **10**, 272 (1971).

(6) I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, **13**, 28 (1960).
(7) D. M. Lemal in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N.Y., 1970, p 345.
(8) (a) G. A. Heath, R. Mason, and K. M. Thomas, *J. Amer. Chem. Soc.*, **96**, 259 (1974); (b) R. Mason, K. M. Thomas, J. A. Zubieta, P. G. Douglas, A. R. Galbraith, and B. L. Shaw, *ibid.*, **96**, 260 (1974).
(9) F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, **16**, 487 (1972); D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).
(10) W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957).
(11) D. M. Lemal, F. Menger, and E. Coats, *J. Amer. Chem. Soc.*, **86**, 2395 (1964).
(12) An aqueous solution of sodium hydroxide may also be used to increase the pH in these steps.
(13) J. G. Atkinson, D. W. Cillis, and R. S. Stuart, *Can. J. Chem.*, **47**, 477 (1969).
(14) A. D. Mighell, A. Santoro, and J. D. H. Donnay, "International Tables for X-Ray Crystallography," Vol. 1, 3rd ed, The Kynoch Press, Birmingham, England, 1969, p 530.
(15) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(16) J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.*, **9**, 2397 (1970).
(17) Other programs used in the solution and refinement included Zalkin's FORDAP Fourier summation program. Woolfson's MULTAN package of direct methods programs, Iber's NUCLS group least-squares refinement program based on Busing and Levy's ORFLS, Busing and Levy's ORFFE, Johnson's ORTEP plotting program, Corfields RANGER weighting analysis program, and the general absorption program AGNOST.[18] All computations were performed on a CDC 6400 computer.
(18) P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Crystallogr.*, **18**, 1035 (1965).
(19) J. A. Ibers, D. H. Templeton, B. K. Vainshtein, G. E. Bacon, and K. Lonsdale, ref 14, Vol. 3, 1962, p 202.
(20) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(21) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
(22) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
(23) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(24) See paragraph at end of paper regarding supplementary material.
(25) H. Wieland and H. Fressel, *Justus Liebigs Ann. Chem.*, **392**, 133 (1912).
(26) S. F. Nelson, R. B. Metzler, and M. Iwamura, *J. Amer. Chem. Soc.*, **91**, 5103 (1969).
(27) G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, **67**, 1655, 1659 (1963).
(28) C. Rømming and K. Waerstand, *Chem. Commun.*, 299 (1965).
(29) H. Ondik and D. Smith, ref 14, 2nd ed, Vol. 3, 1968, p 260.
(30) M. Massaux, M. J. Bernard, and M. Le-Bihan, *Acta Crystallogr., Sect. B*, **27**, 2419 (1971).
(31) R. Graziani, G. Bombieri, and E. Forsellini, *J. Chem. Soc. A*, 2331 (1971).
(32) C. H. Chang, R. F. Porter, and S. H. Bauer, *J. Amer. Chem. Soc.*, **92**, 5313 (1970).
(33) W. H. Beamer, *J. Amer. Chem. Soc.*, **70**, 2979 (1948).
(34) R. M. Curtis and R. A. Pasternak, *Acta Crystallogr.*, **8**, 675 (1955).
(35) R. J. Kurland and E. B. Wilson, Jr., *J. Chem. Phys.*, **27**, 585 (1957).
(36) B. Bak, D. Christensen, L. Hansen, and J. Rastrup-Anderson, *J. Chem. Phys.*. **24**, 720 (1956).
(37) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.
(38) N. V. Sutton, *Anal. Chem.*, **36**, 2120 (1964); R. Preussmann, H. Hengy, and A. von Hodenberg, *Anal. Chim. Acta*, **42**, 95 (1968).
(39) W. M. Tolles, W. R. McBride, and W. E. Thun, *J. Amer. Chem. Soc.*, 91, 2443 (1969).
(40) F. Klages, G. Nober, F. Kircher, and M. Bock, *Justus Liebigs Ann. Chem.*, **547**, 1 (1941).
(41) W. H. Urry, Z. L. F. Gaibel, J. C. Duggan, and S. S. Tseng., *J. Amer. Chem. Soc.*, **95**, 4338 (1973).
(42) A. W. Nineham, *Chem. Rev.*, **55**, 355 (1955).
(43) W. D. Hooper, *Rev. Pure Appl. Chem.*, **19**, 221 (1969).
(44) W. G. Nigh in "Oxidation in Organic Chemistry," W. S. Trahanosky, Ed., Academic Press, New York, N.Y., 1973, p 1.

Synthesis, Crystal Structure, and Magnetic Properties of a Dimeric Quinoline Adduct of Copper(II) Trifluoroacetate

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Abstract: Further synthetic investigations of the copper(II) trifluoroacetate-quinoline system have led to the isolation and characterization of two new products, in addition to the two previously reported. A hygroscopic green crystalline material has been shown by a crystal structure analysis to be the dimeric quinoline adduct $[Cu(O_2CCF_3)_2(quinoline)]_2$. This material hydrolyzes readily to monomeric blue $Cu(O_2CCF_3)_2(quinoline)(H_2O)$. The dimeric complex crystallizes in space group $C\,2/c$ with a = 14.886 (24) Å, b = 16.707 (29) Å, c = 13.694 (23) Å, and β = 111.26 (5) °. Observed and calculated densities are 1.74 (2) and 1.76 g/cm^3, respectively. The structure determination was based upon 1555 independent counter data; anisotropic full-matrix least-squares refinement converged to a conventional R factor of 0.062. The centrosymmetric diquinolinetetra-μ-trifluoroacetato(*O,O'*)-dicopper(II) molecule has the familiar bridged dimeric copper(II) acetate structure with an unusually long Cu-Cu distance of 2.886 (4) Å. Magnetic susceptibility data (85-340°K) conform to the usual dimer equation, with a singlet-triplet energy separation of $2J = -310$ cm^{-1}. The electron paramagnetic resonance spectrum of a polycrystalline sample of the dimer shows a triplet pattern much like that of copper(II) acetate hydrate. The unexpectedly close similarity of the magnetic properties of the acetate and trifluoroacetate adducts forces a reexamination of the hypothesis that the magnitude of metal-metal interaction in these dimers is determined by the strength of the parent carboxylic acid.

A vast number of dimeric copper(II) carboxylate monoadducts, $[Cu(O_2CR)_2L]_2$, have been investigated in an effort to determine the factors influencing the magnitude of the intramolecular magnetic exchange interaction which occurs between the two Cu^{2+} ions in these compounds.[1] One frequently advanced relationship is that between the basicity of the bridging carboxylate anion, as measured by the pK_a of its parent acid, and the magnitude of the exchange coupling constant $2J$.[1,2] Although there is some experimental support for such a correlation, there also exist exceptions[10] to the postulated dependence of $2J$ upon pK_a, and the entire situation must still be regarded as ill-defined. The situation is further complicated by the general disinclination toward formation of the bridged dimeric structure by copper(II) complexes of the stronger carboxylic acids. Thus, the anhydrous copper(II) carboxylates $Cu(O_2CR)_2$ with R = $CHCl_2$, CCl_3, and CF_3 are probably not dimeric[11-13] and these carboxylates tend to form monomeric, magnetically dilute adducts, $Cu(O_2CR)_2L_2$, with most bases.[14-16] For this reason dimeric copper(II) trichloroacetates or trifluoroacetates, which could potentially be important in clarifying the relationship between pK and $2J$, have not been available until very recently.

We have recently shown that the copper(II) trifluoroace-