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The Crystal and Molecular Structure of Bromoazido-1,1,7,7-tetraethyldiethylenetriaminecopper(II)

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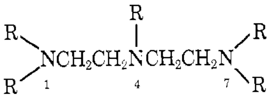
The crystal and molecular structure of bromoazido-1,1,7,7-tetraethyldiethylenetriaminecopper(II), $Cu(Br)N_3(HN((CH_2)_2N(C_2H_5)_2)_2)$, has been determined from three-dimensional X-ray data collected by counter techniques. The structure was refined by full-matrix least-squares methods. The refinement was carried out using 2494 nonzero reflections for which $F^2 > \sigma(F^2)$, and assuming anisotropic thermal motion for all nonhydrogen atoms. The least-squares refinement led to a final value of the conventional R factor (on F) of 0.050. Discrete molecular units of $Cu(Br)N_3(HN((CH_2)_2N(C_2H_5)_2)_2)$ are separated by normal van der Waals distances. The closest Cu-Cu approach is 6.395 (1) Å. The central copper atom is pentacoordinated, and the geometry around the metal atom can be described as a distorted trigonal bipyramid with the bromine atom lying in the equatorial plane and the azido group occupying an apical position. The distortion from ideal trigonal-bipyramidal geometry can be attributed to steric factors, in particular to nonbonded repulsions between the Et_4dien ligand and the Br and N_3 ligands. The closest C–Br contacts are approximately 0.2 Å shorter than the sum of the appropriate van der Waals radii. The Cu–Br distance is unusually long at 2.586 (1) Å and the equatorial Cu–N distances (2.161 (4), 2.224 (4) Å) are appreciably longer than the axial Cu–N distances (1.927 (6), 2.015 (5) Å). The relative elongation of the equatorial Cu–N bonds contrasts with data reported for other chelated trigonal-bipyramidal Cu(II) complexes, where little difference is noted between the axial and equatorial distances. The coordinated azido group is approximately linear with no significant difference in the two independent N–N bond distances which average 1.144 (12) Å. The angle between the copper atom and the bonded azido group is 125.4 (5)°. The monocoordinate azido group in this complex possesses an asymmetric N–N stretching vibration at 2053 cm^{-1}, the same as that reported for the bridging azido groups in $((CuN_3(C_6H_5)_3P)_2)_2$. A summary of structural data on the tetraethyldiethylenetriamine and azido ligands is presented and discussed. Crystal data are as follows: triclinic, space group C_i^1-$P\bar{1}$; $a = 7.683$ (2) Å, $b = 12.848$ (1) Å; $c = 9.916$ (1) Å, $\alpha = 111.67$ (2)°, $\beta = 99.54$ (2)°, $\gamma = 93.14$ (3)° (temperature 22°); $Z = 2$; $d_{obsd} = 1.58$ g/cm³, $d_{calcd} = 1.59$ g/cm³.

Introduction

The role of the tridentate ligands 1,1,7,7,-tetraethyldiethylenetriamine (Et_4dien) and 1,1,4,7,7,-pentamethyldiethylenetriamine (Me_5dien)[2] in forming four- and five-coordinate metal complexes and in demonstrating pronounced stereochemical effects has been well established both in the solution and solid states.[3-6] In the solid state, investigations have centered around the high-spin five-coordinate complexes of the first-row transition metal ions, particularly those of Ni(II)[7] and Co(II).[8-10] It has been demonstrated that whereas Me_5dien forms high-spin five-coordinate $NiLX_2$ complexes in the solid state, Et_4dien, due to its relative bulkiness, forms low-spin four-coordinate [NiLX]X complexes in both solid and solution states.[7] The effect of the counter anion (X) in determining the coordination number of the central metal ion in these complexes has also been studied.[11]



$$\underset{1}{R_2N}CH_2CH_2\underset{4}{\overset{R}{N}}CH_2CH_2\underset{7}{NR_2}$$

We have extended the study of structural effects of these ligands to a series of complexes containing copper as the central metal ion. Physical and chemical data suggest that the complexes are five-coordinate in the solid state.[12] To illustrate the nature of the coordination and the extent of the stereochemical effect of the bulky Et_4dien ligand, we report here the structural results for a representative compound of the series, $Cu(Br)N_3(HN((CH_2)_2N(C_2H_5)_2)_2)$.[13]

Experimental Section

Preparation of the Complex.—Ten milliliters of a methanol solution containing 0.012 mol of 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien) was added to 100 ml of a hot methanol solution containing 0.01 mol $CuBr_2$. Addition of 30 ml of *n*-butyl alcohol followed by evaporation of the methanol and cooling gave a stoichiometric yield of black crystalline $CuBr_2(Et_4dien)$. A methanol solution (10 ml) containing 0.01 mol of $CuBr_2(Et_4dien)$ was added to 200 ml of a hot methanol solution containing 0.01 mol of NaN_3 and the resulting mixture stirred for 10 min. Addition of 50 ml of *n*-butyl alcohol followed by evaporation of the methanol caused the precipitation of NaBr. The solution was filtered and cooled whereupon $Cu(Br)N_3(Et_4dien)$ precipitated. The complex may be recrystallized from a methylene chloride–isopropyl alcohol or acetonitrile solution.

Collection and Reduction of Intensity Data

Suitable dark green crystals of $Cu(Br)N_3(Et_4dien)$ were obtained by recrystallization from an acetonitrile solution. A series of Weissenberg and precession photographs taken with Mo K$\bar{\alpha}$ and Cu K$\bar{\alpha}$ radiations revealed no symmetry elements. Hence, the crystals were assigned to the triclinic system.

The initial cell constants were obtained from a least-squares refinement based on 2θ values obtained from precision Weissenberg photographs taken at 22°. The independent intensity data set was collected from a single crystal at 22° using a Datex-automated General Electric XRD-6 diffractometer. The crystal was mounted with its a axis approximately parallel to the ϕ axis of the diffractometer and had the dimensions 0.08 × 0.09 × 0.12 mm.

Sixteen reflections ($2\theta < 50°$) were centered in the counter

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[2] The ligands are also named and sold as *N,N*-bis(β-diethylaminoethyl)amine and *N,N*-bis(β-dimethylaminoethyl)methylamine, respectively.

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aperture by varying 2θ, ϕ, and χ in conjunction with the left–right and top–bottom balancing features of the variable receiving aperature. The cell constants and their standard deviations were determined by a least-squares refinement of the 2θ values for these 16 reflections. The results (Cu $K\bar{\alpha}$ radiation, $\lambda = 1.5418$) are $a = 7.683$ (2), $b = 13.012$ (1), $c = 9.916$ (1) Å; and $\alpha = 113.42$ (2), $\beta = 80.46$ (2), $\gamma = 100.39$ (3)° (at 22°). The calculated density of 1.59 g/cm^3 for two fomula units in the cell agrees with the observed density of 1.58 g/cm^3 obtained by the flotation method (CCl_4–C_6H_6). A Delaunay reduction to obtain a cell with all angles obtuse revealed no hidden symmetry. The results for the final cell constants and their standard deviations are $a = 7.683$ (2), $b = 12.848$ (1), $c = 9.916$ (1) Å; and $\alpha = 111.67$ (2), $\beta = 99.54$ (2), $\gamma = 93.14$ (3)° at 22°. A second independent reduction using the algorism of Balashov and Ursell[14] revealed that the Delaunay reduced cell is identical with the Dirichlet reduced cell. Hence the cell axes represent the three shortest noncoplanar translations (Dirichlet triplet). The corresponding ϕ and χ values for the 16 reflections were used as input data for the orientation program operating under the CRYM crystallographic computing system.

A total of 3508 independent reflections were collected by the θ–2θ scan techique in the range $4° \leq 2\theta$ (Cu $K\bar{\alpha}$) $\leq 157°$. A takeoff angle of 3° was used with the counter wide open. A check of several high-angle reflections indicated that our settings included the entire peak in the scan. The pulse height analyzer was set for approximately a 90% window centered on the Cu $K\alpha$ peak. A scan rate of 2°/min (in 2θ) was used with stationary counter, stationary crystal background counts of 30 sec duration taken at each end of the scan. A symmetric scan range of between 2 and 3.4° was adjusted to account for $\alpha_1 - \alpha_2$ splitting.

Throughout the data collection the intensities of three reference reflections were measured every 60 reflections to monitor the crystal's stability. The average intensity of the three reflections decreased linearly over the 260 hr collection period by approximately 16% of its original value. The decomposition was isotropic and a linear correction factor for decomposition was applied to the intensity data.

The values for the observed intensities, I_{obsd}, were derived from the scalar counts using the formula

$$I_{\text{obsd}} = S - \frac{B_1 + B_2}{2}\left(\frac{t}{30}\right)$$

where S is the scan count, B_1 and B_2 are the two background counts, and t is the scan time in seconds. Negative values of I_{obsd} calculated from this formula were set equal to zero. The standard deviation for each reflection was calculated using

$$\sigma^2(I_{\text{obsd}}) = S + \frac{B_1 + B_2}{2}\left(\frac{t}{30}\right)^2 + (0.02S)^2$$

The last term in this equation is an empirical term (Busing and Levy)[15] which presumably allows for errors not due to counting statistics. The standard deviations calculated in this way were the basis for the weights used in the least-squares refinement. The intensities and their standard deviations were corrected for Lorentz and polarization effects but not for absorption. The linear absorption coefficient (Cu $K\alpha$) for this compound is 50 cm^{-1}, and the transmission coefficients for the selected crystal range from 0.64 to 0.55. Neglect of absorption effects could have led to errors in the relative values of the structure factors amounting to about 6% in the extreme case.[16] The data were put on an approximately absolute scale with a Wilson plot.[17] The result of a tabulation of E statistics[18] and of an application of the zero moment test of Howells, Phillips, and Rogers[19] suggested the centric space group $P\bar{1}$. Of the 3508 reflections collected, 2494 obeyed the condition $F^2 > \sigma(F^2)$ and were used in subsequent calculations.

Elucidation and Refinement of the Structure

Heavy-atom methods were applied to solve the structure. The positions of the copper and bromine atoms were readily determined from a three-dimensional Patterson function calculation. Structure factors calculated on the basis of the coordinates of these atoms led to an R index ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.301. Subsequent Fourier maps were used to locate the remaining nonhydrogen atoms. Three cycles of full-matrix least-squares refinement of the coordinates and isotropic temperature factors of all the nonhydrogen atoms reduced the R index to 0.095. Introduction of anisotropic temperature factors for all these atoms at this point further reduced the R index to 0.082. The hydrogen atom positions were located on a difference Fourier map in conjunction with calculations based upon tetrahedral geometry for the methylene and methyl carbon atoms and for the nitrogen atom. Each hydrogen atom was assigned an isotropic temperature factor one unit higher than the value of the last refined isotropic temperature factor for the atom to which the hydrogen was attached. Inclusion of the hydrogen parameters in the least-squares refinement reduced the R index to 0.067. At this point the F_o value for two reflections, 100 and $00\bar{1}$, was corrected to account for a truncation error which occurred during collection of the intensity data. Subsequent refinement reduced the R index to 0.054.

A comparison of the F_o and F_c values for several low-angle reflections suggested the presence of a secondary extinction effect and in the final least-squares cycles 298 parameters were adjusted; these included a scale factor, a secondary extinction factor,[20a] positional parameters of all of the 49 atoms, anisotropic temperature factors for the nonhydrogen atoms, and isotropic temperature factors for the hydrogen atoms. The 298 parameters were apportioned among four complete matrices due to storage limitations of the computer.

All calculations were carried out on an IBM 370-155 computer using subprograms operating under the CRYM crystallographic computing system. The quantity minimized throughout the least-squares refinement was $\Sigma w(F_o^2 - F_c^{*2})^2$, where $w = 1/\sigma^2(F_o^2)$ and F_c^* is as defined by Larson's eq 3.[20b] Atomic form factors for Br, Cu, C, and N were taken from Hansen, Herman, Lea, and Skillman,[21] the values for Br and Cu being reduced by 0.96 and 2.15 electrons, respectively, to take account of the real part of anomalous dispersion.[22] $\Delta f''$ was ignored. The atomic form factor for hydrogen used was that calculated by Stewart, Davidson, and Simpson.[23]

In the final cycle of refinement no heavy-atom parameter shifted by as much as 0.4 esd. The final R index for 2494 reflections above σ was 0.050, and the goodness of fit, $[\Sigma w(F_o^2 - F_c^2)^2/(m - s)]^{1/2}$, where m is the number of reflections and s the number of refinable parameters, was 1.67. The final value of the secondary extinction parameter, g, as defined by Larson's eq 3,[20b] was $(1.42 \pm 0.19) \times 10^{-6}$. Inclusion of the secondary extinction correction in the refinement reduced R and R' by 0.004 and 0.002, respectively, with the final value for R' ($R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$) being 0.012. On a final difference Fourier synthesis the highest peak was 0.40 e/Å^3 as compared with the value 2.5 e/Å^3 for a typical carbon atom and 0.6 e/Å^3 for a typical hydrogen atom in this structure. The final parameters and their estimated standard deviations for the heavy atoms and for the hydrogen atoms are given in Table I and Table II, respectively. The values of the observed and calculated structure factors (in e × 10) are available.[24]

The estimated standard deviations in the positions of the bromine and copper atoms are approximately 0.001 Å while those for the carbon and nitrogen atoms are about 0.008 Å, except for the two atoms (N(3) and C(1)) whose vibrational amplitudes exceed 0.4 Å.

The Molecular Structure

Bromoazido-1,1,7,7-tetraethyldiethylenetriaminecop-

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(24) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number INORG-72-3044. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE I

POSITIONAL AND THERMAL PARAMETERS OF THE HEAVY ATOMS[a,b]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.55904 (10)	0.28018 (6)	0.07226 (9)	0.00142 (2)	0.00613 (7)	0.01219 (12)	0.00223 (17)	0.00498 (22)	0.00867 (15)
Br	0.35396 (9)	0.43638 (6)	0.14573 (8)	0.02045 (16)	0.00784 (6)	0.02040 (13)	0.01039 (15)	0.01503 (22)	0.01482 (14)
N(1)	0.4049 (7)	0.1565 (4)	0.0718 (6)	0.0182 (11)	0.0076 (4)	0.0206 (9)	0.0010 (11)	0.0081 (17)	0.0140 (10)
N(2)	0.2527 (8)	0.1477 (4)	0.0486 (7)	0.0171 (11)	0.0080 (5)	0.0290 (12)	0.0026 (12)	0.0071 (20)	0.0186 (12)
N(3)	0.1008 (9)	0.1336 (7)	0.0294 (12)	0.0173 (15)	0.0181 (9)	0.0812 (33)	0.0023 (20)	0.0073 (37)	0.0514 (30)
N(4)	0.5846 (6)	0.1859 (4)	−0.1530 (5)	0.0194 (11)	0.0074 (4)	0.0123 (7)	0.0054 (10)	0.0063 (14)	0.0099 (9)
N(5)	0.7457 (6)	0.3924 (4)	0.0630 (5)	0.0159 (9)	0.0058 (4)	0.0159 (7)	0.0023 (9)	0.0086 (14)	0.0101 (9)
N(6)	0.7407 (6)	0.3009 (4)	0.2824 (5)	0.0171 (10)	0.0066 (4)	0.0118 (7)	0.0028 (9)	0.0039 (13)	0.0078 (8)
C(1)	0.7191 (14)	0.0093 (7)	−0.2887 (9)	0.0288 (9)	0.0105 (7)	0.0197 (13)	0.0199 (25)	0.0368 (34)	0.0115 (16)
C(2)	0.6731 (9)	0.0871 (5)	−0.1464 (7)	0.0146 (7)	0.0066 (5)	0.0139 (9)	0.0078 (14)	0.0096 (20)	0.0083 (11)
C(3)	0.4094 (10)	0.1432 (6)	−0.2606 (7)	0.0265 (7)]	0.0126 (7))	0.0133 (10)	0.0030 (18)	−0.0056 (21)	0.0082 (14)
C(4)	0.2905 (11)	0.2317 (8)	−0.2545 (9)	0.0254 (9)	0.0194 (11)	0.0210 (14)	0.0107 (25)	−0.0068 (27)	0.0207 (21)
C(5)	0.6971 (9)	0.2635 (5)	−0.1914 (7)	0.0313 (18)	0.0081 (5)	0.0134 (9)	0.0094 (16)	0.0164 (21)	0.0117 (12)
C(6)	0.8381 (9)	0.3349 (5)	−0.0586 (7)	0.0213 (14)	0.0086 (5)	0.0201 (1)	0.0070 (14)	0.0198 (21)	0.0170 (13)
C(7)	0.8634 (8)	0.4505 (5)	0.2122 (5)	0.0164 (13)	0.0077 (5)	0.0166 (10)	−0.0031 (13)	0.0027 (18)	0.0088 (12)
C(8)	0.9064 (9)	0.3615 (6)	0.2754 (7)	0.0175 (14)	0.0097 (6)	0.0175 (11)	−0.0029 (14)	−0.0052 (19)	0.0119 (13)
C(9)	0.9057 (11)	0.1863 (7)	0.4134 (8)	0.0325 (21)	0.0155 (8)	0.0179 (12)	0.0166 (21)	0.0047 (25)	0.0197 (17)
C(10)	0.7733 (8)	0.1877 (5)	0.2820 (7)	0.0217 (15)	0.0092 (5)	0.0147 (9)	0.0084 (17)	0.0056 (19)	0.0130 (12)
C(11)	0.6721 (10)	0.3704 (5)	0.4156 (7)	0.0304 (18)	0.0087 (6)	0.0125 (9)	0.0076 (16)	0.0059 (21)	0.0071 (12)
C(12)	0.5022 (11)	0.3183 (6)	0.4352 (8)	0.0382 (23)	0.0114 (7)	0.0164 (11)	0.0099 (20)	0.0251 (26)	0.0127 (14)

[a] The estimated standard deviations in the least significant figure(s) as derived from the inverse matrix of the final least-squares refinement cycle are given in parentheses. [b] The temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

TABLE II

POSITIONAL AND THERMAL PARAMETERS OF THE HYDROGEN ATOMS[a,b]

Atom	x	y	z	B
H(1)(C(1))	0.775 (10)	0.039 (7)	−0.331 (8)	10.7 (22)
H(2)	0.752 (10)	−0.049 (7)	−0.274 (9)	11.2 (22
H(3)	0.601 (10)	−0.041 (6)	−0.364 (8)	9.8 (22)
H(4)(C(2))	0.581 (7)	0.043 (5)	−0.102 (6)	5.3 (14)
H(5)	0.764 (7)	0.115 (4)	−0.082 (6)	4.2 (13)
H(6)(C(3))	0.336 (7)	0.082 (5)	−0.234 (6)	4.8 (14)
H(7)	0.440 (8)	0.106 (5)	−0.348 (6)	5.9 (15)
H(8)(C(4))	0.351 (10)	0.301 (6)	−0.246 (8)	9.6 (20)
H(9)	0.187 (10)	0.208 (6)	−0.325 (8)	9.7 (21)
H(10)	0.257 (10)	0.257 (6)	−0.167 (8)	9.7 (21)
H(11)(C(5))	0.742 (7)	0.224 (4)	−0.281 (5)	4.8 (14)
H(12)	0.624 (8)	0.324 (5)	−0.217 (6)	5.5 (14)
H(13)(C(16))	0.910 (6)	0.386 (4)	−0.082 (5)	3.2 (11)
H(14)	0.919 (7)	0.289 (4)	−0.034 (5)	3.9 (12)
H(15)(C(7))	0.763 (9)	0.504 (6)	0.264 (7)	7.9 (17)
H(16)	0.975 (5)	0.476 (3)	0.199 (4)	1.0 (7)
H(17)(C(8))	0.984 (8)	0.403 (5)	0.370 (6)	5.5 (14)
H(18)	0.989 (9)	0.294 (6)	0.205 (7)	8.3 (17)
H(19)(C(9))	0.859 (9)	0.233 (5)	0.513 (7)	7.5 (17)
H(20)	0.998 (9)	0.217 (6)	0.413 (7)	8.6 (19)
H(21)	0.896 (9)	0.108 (6)	0.399 (7)	7.5 (18)
H(22)(C(10))	0.814 (7)	0.147 (4)	0.197 (5)	3.0 (11)
H(23)	0.671 (7)	0.136 (4)	0.264 (6)	3.9 (12)
H(24)(C(11))	0.640 (8)	0.439 (5)	0.397 (6)	5.1 (14)
H(25)	0.769 (7)	0.386 (4)	0.514 (6)	4.5 (13)
H(26)(Cl(12))	0.495 (9)	0.256 (6)	0.441 (7)	7.1 (17)
H(27)	0.396 (9)	0.285 (5)	0.328 (7)	7.6 (18)
H(28)	0.482 (9)	0.373 (6)	0.526 (8)	8.4 (18)
H(29)(N(5))	0.672 (8)	0.437 (5)	0.027 (6)	6.9 (15)

[a] See footnote *a*, Table I. [b] Hydrogen atoms are bonded to the atom given in parentheses. No designation indicates bonding to the atom in parentheses immediately above the hydrogen.

TABLE III

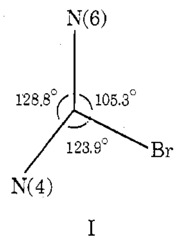
INTRAMOLECULAR DISTANCES (Å) AND ANGLES (DEG)[a,b]

Atoms	Distances	Atoms	Angles
Cu–Br	2.586 (1)	Br–Cu–N(1)	98.8 (2)
Cu–N(1)	1.927 (6)	Br–Cu–N(4)	123.9 (1)
Cu–N(4)	2.161 (4)	Br–Cu–N(5)	89.8 (1)
Cu–N(5)	2.015 (5)	Br–Cu–N(6)	105.3 (1)
Cu–N(6)	2.224 (4)	N(1)–Cu–N(4)	91.5 (2)
N(1)–N(2)	1.145 (8)	N(1)–Cu–N(5)	171.4 (2)
N(2)–N(3)	1.144 (9)	N(1)–Cu–N(6)	94.2 (2)
N(4)–C(2)	1.490 (8)	N(4)–Cu–N(5)	83.4 (2)
N(4)–C(3)	1.504 (8)	N(4)–Cu–N(6)	128.8 (2)
N(4)–C(5)	1.476 (9)	N(5)–Cu–N(6)	83.8 (2)
N(5)–C(6)	1.478 (8)	Cu–N(1)–N(2)	125.4 (5)
N(5)–C(7)	1.494 (7)	N(1)–N(2)–N(3)	175.5 (10)
N(6)–C(8)	1.481 (8)	N(4)–C(5)–C(6)	110.2 (6)
N(6)–C(10)	1.488 (9)	N(5)–C(6)–C(5)	107.2 (5)
N(6)–C(11)	1.494 (8)	N(5)–C(7)–C(8)	107.8 (4)
C(1)–C(2)	1.508 (10)	N(6)–C(8)–C(7)	110.4 (5)
C(3)–C(4)	1.488 (12)	N(4)–C(2)–C(1)	116.3 (6)
C(5)–C(6)	1.509 (8)	N(4)–C(3)–C(4)	114.0 (5)
C(7)–C(8)	1.520 (11)	N(6)–C(10)–C(9)	116.4 (5)
C(9)–C(10)	1.519 (10)	N(6)–C(11)–C(12)	115.1 (5)
C(11)–C(12)	1.509 (12)	C(2)–N(4)–C(3)	108.6 (4)
Br–C(4)	3.796 (5)	C(6)–N(5)–C(7)	115.3 (4)
Br–C(11)	3.685 (6)	C(10)–N(6)–C(11)	112.2 (5)
Cu–Cu[c]	6.395 (1)	C(4)–Br–C(11)	90.1 (4)

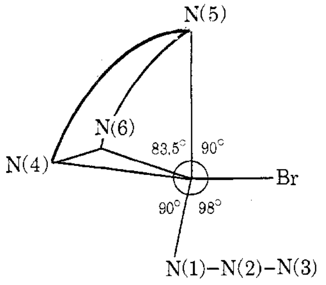
[a] See Figure 2 for the atom-labeling scheme. [b] Values in parentheses are estimated standard deviations in the last digits as derived from the inverse matrix of the final least-squares refinement cycle. [c] Closest Cu–Cu approach $[1 - x, 1 - y, \bar{z}]$. The Cu–Cu distance within the unit cell $[1 - x, 1 - y, 1 - z]$ is 8.510 (1) Å.

per(II) exists as discrete monomeric molecular units in the solid state. The closest Cu–Cu approach is 6.395 (1) Å, being between the two copper atoms lying approximately in the (001) plane as may be seen in Figure 1. Interatomic distances and angles are summarized in Table III.

The copper atom in the molecule is five-coordinate. The geometry of the coordination sphere of copper is a distorted trigonal bypyramid (Figures 2 and 3) with the bromine atom lying in the equatorial plane and the coordinated azido group occupying an apical position of the bipyramid. Table IV gives two least-squares planes (A, through N(4), Br, N(6), and Cu;



I



II

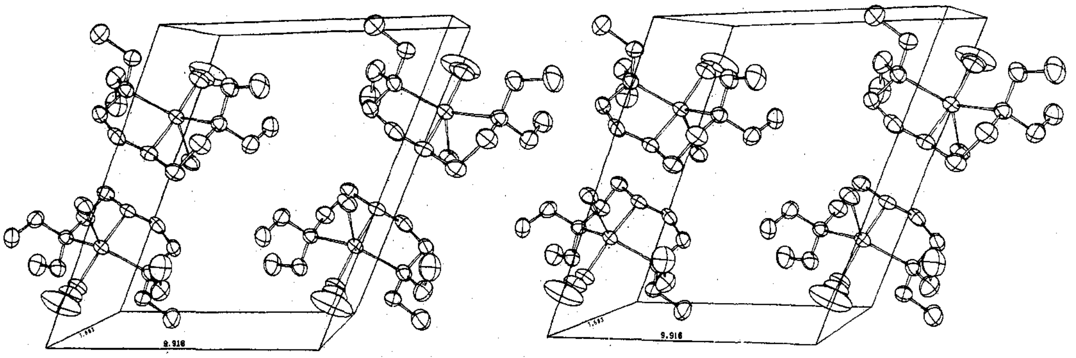


Figure 1.—A stereoscopic view of the molecular packing in a unit cell of $Cu(Br)N_3(HN((CH_2)_2N(C_2H_5)_2)_2)$. $a = 7.683\ (2)$, $b = 12.848\ (1)$, and $c = 9.916 (1)$ Å.

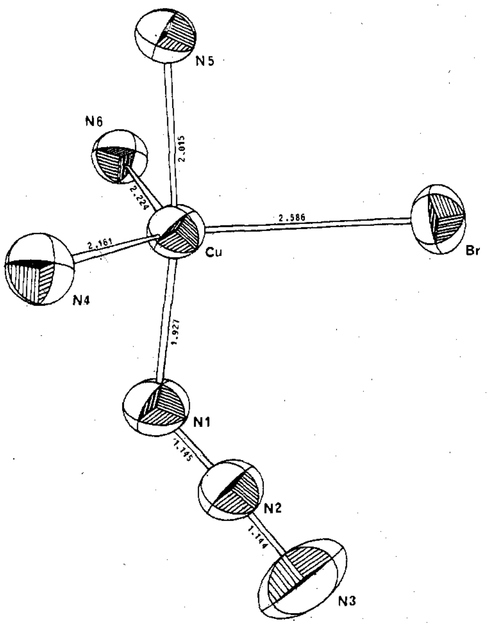


Figure 2.—Inner coordination sphere of $Cu(Br)N_3(HN((CH_2)_2N(C_2H_5)_2)_2)$. The 40% probability ellipsoids are shown here and in Figures 1 and 3.

TABLE IV

LEAST-SQUARES PLANES IN THE $Cu(Br)N_3(HN((CH_2)_2N(C_2H_5)_2)_2)$ MOLECULE[a–c]

Atom	Dev, Å	Atom	Dev, Å
Plane A: $0.6319\mathbf{X} + 0.7742\mathbf{Y} - 0.0353\mathbf{Z} - 5.200 = 0$			
Br*	+0.036	Cu*	−0.136
N(4)*	+0.055	N(1)	−2.056
N(6)*	+0.045	N(5)	+1.874
Plane B: $0.6293\mathbf{X} + 0.7765\mathbf{Y} - 0.0326\mathbf{Z} - 5.246 = 0$			
Br*	0.0	Cu	−0.183
N(4)*	0.0	N(1)	−2.103
N(6)*	0.0	N(5)	+1.827

[a] Planes are defined in the real triclinic coordinates (**X**, **Y**, **Z**). [b] Planes are calculated using unit weights for atoms marked with an asterisk. [c] The interplanar angle AB is 0.5°.

B, through N(4), Br, and N(6)). The Cu atom is displaced out of plane B by about 0.2 Å toward the azido ligand (N(1)). The angles between the Cu atom and the three atoms of the equatorial plane deviate from 120° as shown in I, while the axis of the bipyramid deviates from linearity (N(1)–Cu–N(5) angle = 171.4 (2)°) and is bent in a direction away from the Br atom (II).

The distortion from ideal trigonal-bipyramidal geometry apparently results because of nonbonded repulsions between Et_4dien and the Br and N_3 ligands. A listing of the nonbonded contacts between appropriate ligand-atom pairs is given in Table V. Significant nonbonded repulsions occur between the Br atom and the methyl or methylene groups of the Et_4dien ligand where the Br–C distances involving carbons 4, 11, and 12 are all approximately 0.2 Å shorter than the sum of the appropriate van der Waals radii.[25a] The relief from steric strain is most apparent in the unusually long Cu–Br distance of 2.586 (1) Å, which is approximately 0.3 Å greater than the sum of the individual atomic radii.[25] The Br–N(1), Br–N(2), and N(2)–C(3) contacts are equal to the sum of the corresponding van der Waals radii and reflect the tight packing of the coordinated end of the azido group. Similar distortions due to steric effects have been observed in the structure of the five-coordinate complex $CoCl_2(Et_4dien)$.[9] Steric repulsions also appear to play a role in determining the placement of the ligands about the five-coordinate Co atom in $CoCl_2(Me_5dien)$.[8] We rule out the possibility that the distortion from ideal geometry in the present case is due to internal strain in the Et_4dien ligand, since Dori[4] has shown that in the complex $[Ni(NCS)(Et_4dien)]I$ the nickel atom and three nitrogen atoms of the tridentate ligand are coplanar.

TABLE V

NONBONDED CONTACTS (IN Å) WITHIN THE $Cu(Br)N_3(Et_4dien)$ MOLECULE

Br–C(X)		Br–N(X)		N(1)–C(X)	
X = 4:	3.796 (5)	X = 1:	3.453 (6)	X = 2:	3.159 (8)
11:	3.685 (6)	2:	3.477 (7)	3:	3.243 (9)
12;	3.763 (5)	5:	3.273 (7)	10:	3.137 (9)
				12:	3.357 (9)
Sum of the Appropriate van der Waals Radii, Å[a]					
	3.95		3.45		3.5

[a] Reference 25a; the methyl radius is used for C(X).

A very significant structural feature of the $Cu(Br)N_3(Et_4dien)$ molecule is the elongation of the equatorial Cu–N bonds, as shown by the differences in the Cu–N distances involving the tridentate and azido ligands. The two apical Cu–N distances (–N(1), 1.927 (6) Å;

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(25) (a) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260. (b) The equatorial Cu–Br distance in $CuBr_5^{3-}$ is 2.519 (2) Å. (K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).)

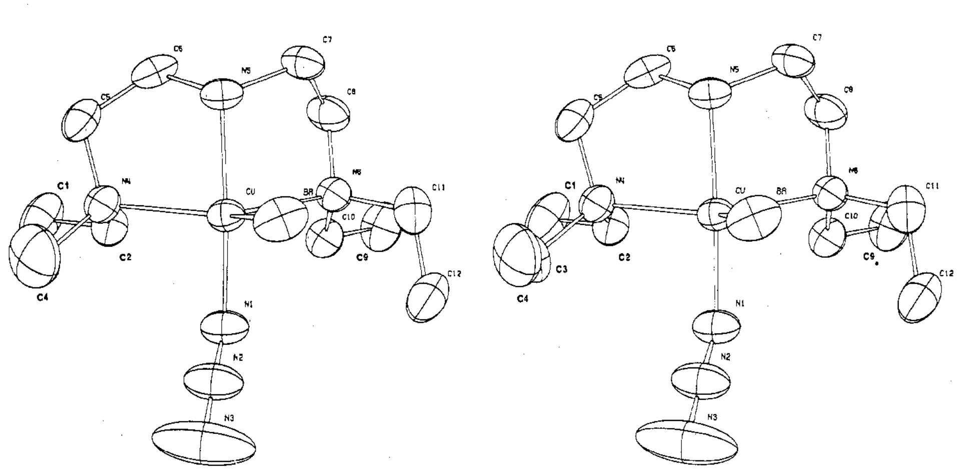

Figure 3.—A stereoscopic view of the molecule Cu(Br)N$_3$(HN((CH$_2$)$_2$N(C$_2$H$_5$)$_2$)$_2$). Hydrogen atoms have been omitted for the sake of clarity.

TABLE VI

COMPARISON OF AXIAL AND EQUATORIAL M–L BOND DISTANCES IN SOME CHELATED AND NONCHELATED TRIGONAL-BIPYRAMIDAL Cu(II) COMPLEXES

Complex	Axial distances, Å		Equatorial distances, Å	
[Cu(NCS)(tren)]SCN[a]	Cu–N	2.04	Cu–N	2.07
	Cu–N	1.95	Cu–N	2.16
			Cu–N	2.06
α-[Cu(NCS)(tetramine)]SCN[b]	Cu–N(1)	1.97	Cu–N(2)	2.05
	Cu–N(3)	2.00	Cu–N(4)	2.03
			Cu–N(5)	2.16
Cu(Br)N$_3$(Et$_4$dien)[c]	Cu–N(1)	1.927 (6)	Cu–N(4)	2.161 (4)
	Cu–N(5)	2.015 (5)	Cu–N(6)	2.224 (4)
			Cu–Br	2.586 (1)
CuCl$_2$(dimim)$_3$[d]	Cu–N(53)	2.004 (5)	Cu–N(43)	2.145 (5)
	Cu–N(63)	2.014 (5)	Cu–Cl(3)	2.421 (2)
			Cu–Cl(4)	2.364 (2)
[Cr(NH$_3$)$_6$][CuBr$_5$][e]	Cu–Br(all)	2.4500 (22)	Cu–Br(all)	2.5191 (17)

[a] Reference 28. [b] Reference 30. [c] This work. [d] Reference 36; dimim = 1,2-dimethylimidazole; the values reported here are for one of the two crystallographically independent molecules. [e] Reference 34.

–N(5), 2.105 (5) Å) are not unusual, although the former is somewhat short, and agree with Cu–N distances found in, for example, Cu$_2$(N$_3$)$_2$(diphos)$_3$[26] and Cu(en)$_2$(NO$_3$)$_2$.[27] On the other hand, the equatorial Cu–N(4) and Cu–N(6) distances are long at 2.146 (4) and 2.22 (4) Å, respectively. These results contrast with data obtained for other five-coordinate trigonal-bipyramidal copper(II) chelates, [Cu(NCS)tren][SCN],[28] [CuI(dipy)$_2$]I,[29] and [Cu(NCS)(tetramine)]SCN,[30] which show little difference between axial and equatorial bond lengths for the same type of atom. The average Cu–N distances in these complexes are 2.04, 2.01, and 2.06 Å, respectively. Interestingly, our observation of shorter axial Cu–N bond lengths in Cu(Br)N$_3$(Et$_4$dien) agrees with structural results on trigonal-bipyramidal copper complexes involving *nonchelating* ligands.[31] The few X-ray structural determinations of complexes of the latter type[32,33] have shown that for a given Cu–X bond the axial distance is shorter than the equatorial distance.[34,35] The difference between the axial and equatorial Cu–N bond distances in Cu(Br)N$_3$(Et$_4$dien) is even greater than that reported for the nonchelated CuCl$_2$(dimim)$_3$,[36] but with such large steric effects we cannot evaluate the importance of axial and equatorial d-orbital bonding factors in the former case. Table VI compares axial and equatorial distances in some related chelated and nonchelated complexes.

The Coordinated Azide.—The coordinated azido group is approximately linear with an N–N–N angle of 175.5 (10)°, and symmetrical with the N(1)–N(2) and N(2)–N(3) distances essentially equal at 1.144 (12) Å. The N–N distances fall within the range of the average ionic azide N–N distance of 1.154 ± 0.015 Å suggested by Evans, Yoffe, and Gray.[37] The Cu–N(1)–N(2) angle is 125.4 (5)°, as anticipated for a trigonally hybridized nitrogen atom, in agreement with the M–N–N

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(27) Y. Komiyama and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 1145 (1964).

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(30) N. A. Bailey, E. D. McKenzie, and J. R. Mullins, *Chem. Commun.*, 1103 (1970).

(31) The recently reported bis(1,3-diaminopropane)isothiocyanatocopper(II) perchlorate appears to be the only other trigonal-bipyramidal copper(II) chelate that shows a significant difference between axial and equatorial bond distances. (M. Cannas, G. Carta, and G. Morongier, *Chem. Commun.*, 673 (1971).) In the case of [N$_6$P$_6$(N(CH$_3$)$_2$)$_{12}$CuCl][CuCl$_2$] which has an intermediate geometry between square pyramidal and trigonal bipyramidal the difference between the "axial" and "equatorial" bond distances may be significant. (W. C. Marsh and J. Trotter, *J. Chem. Soc. A*, 1482 (1971).)

(32) (a) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970); (b) B. J. Hathaway, *Essays Chem.*, **2**, 61 (1971).

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(37) B. L. Evans, A. D. Yoffe, and P. Gray, *Chem. Rev.*, **59**, 515 (1959).

TABLE VII

A SUMMARY OF DATA INVOLVING THE –N–C–C–N– UNIT OF THE 1,1,7,7-TETRAETHYLDIETHYLENETRIAMINE LIGAND (Et_4dien)

	Atoms	Dihedral angle,[a] deg	Interchelate N–M–N angle, deg (ligand "bite")	C atom displacement from N–M–N plane
$Cu(Br)N_3(Et_4dien)$	(Present structure)			
	N(4)–C(5)–C(6)–N(5)	44.1	83.4 (2)	C(5), −0.224; C(6), +0.480
	N(5)–C(7)–C(8)–N(6)	57.3	83.8 (2)	C(7), −0.408; C(8), +0.314
$CoCl_2(Et_4dien)$[b]				
	N(1)–C(12)–C(11)–N(2)	55.8	80.1 (3)	C(12), +0.318; C(11), −0.422
	N(2)–C(10)–C(9)–N(3)	50.8	80.7 (2)	C(10), −0.417; C(9), +0.199
$[Ni(NCS)(Et_4dien)]I$[c]				
	N(1)–C(1)–C(2)–N(2)	50.1	86.4 (3)	C(1), −0.17; C(2), −0.76

[a] The dihedral angle is defined as the angle between the lines projecting the atom 1–atom 2 and the atom 4–atom 3 bonds onto a plane which is normal to the atom 2–atom 3 bond. [b] Reference 9; atom numbers are those in the reference. [c] Reference 5; atom numbers are those in the reference. The other –N–C–C–N– unit of the ligand in this complex is related to the one presented by a mirror plane.

angle found in $[Co(NH_3)_5N_3]^{2+}$,[38] $[Fe(N_3)_5]^{2-}$,[39] and $Cu(N_3)_2(C_5H_5N)_2$.[40]

The question of the structural nature of the azido group in coordination compounds has recently been discussed.[26,41,42] The first structural investigation of an azido complex showed that the two N–N bonds of the azido group were of unequal length.[38] Structurally similar azides have since been found in *sym*-$[Co(trenen)N_3](NO_3)_2 \cdot H_2O$[43] and $Cu_2(N_3)_2(diphos)_3$.[26] Other structures such as that of $Zn(N_3)_2(C_5H_5N)_2$[44] have been reported in which the limits of accuracy leave the question of the asymmetry of the azide unresolved. On the other hand, three complexes in addition to $Cu(Br)N_3(Et_4dien)$ have been found to contain symmetric, monocoordinate azido groups. In the pentaazidoferrate(III) ion,[39] $Fe(N_3)_5^{2-}$, the average N–N distance is 1.16 (3) Å and in $[Ru(N_3)(N_2)(en)_2]PF_6$[42] the N–N distances average 1.162 (23) Å. In $[Cu(N_3)(P(C_6H_5)_3)_2]_2$,[45] two coordinated azido groups bridge two copper atoms through the terminal nitrogen atoms (αN, γN) and have an average N–N distance of 1.178 (12) Å. In only the latter case is it easy to rationalize the presence of a symmetric azido group.

The asymmetric N–N stretching frequency (solid state) for the bridging azido compound mentioned above[45,46] is the same as that for $Cu(Br)N_3(Et_4dien)$[12] (ν_3, 2053 cm^{-1}). This comparison shows that the coordination mode of the azido ligand cannot be established solely from a consideration of the asymmetric N–N stretching frequency. Both compounds also exhibit a weak band in their infrared spectra at 1266 cm^{-1}. This band has been assigned previously as the symmetric N–N stretching frequency ν_1 in $(CuN_3((C_6H_5)_3P)_2)_2$.[46] We have assigned ν_1 to a band at 1334 cm^{-1} in the Raman spectrum of $(CuN_3((C_6H_5)_3P)_2)_2$ but $CuBr(N_3)(Et_4dien)$ decomposed in the laser beam.[47] A ν_1 value of 1334 cm^{-1} is reasonable for a symmetric azide, falling between the ν_1 values reported for RbN_3 and CsN_3.[48]

The Et_4dien Ligand.—Bond distances and angles within the Et_4dien ligand appear normal. The eight C–N distances have a mean value of 1.488 (10) Å and the six C–C distances have a mean value of 1.509 (14) Å. The maximum deviation from the tetrahedral angle of 109° for the bond angles around the carbon and nitrogen atoms (excluding hydrogen) is 7°. The overall conformation of the ligand is illustrated in Figure 3. The N–C–C–N ligand grouping has a *gauche* conformation as has been found in all other complexes containing this unit.[49] If the C–N bonds at each end of the N–C–C–N unit of the ligand are projected onto a plane which is normal to the C–C bond, the angles between the projected lines in the present structure are 44.1 and 57.3°. These angles compare favorably with the values given in Table VII for the other known structures containing the Et_4dien ligand.[5,9] The N(5)–Cu–N(4,6) angles do not differ significantly and average 83.6 (3)°. These angles, which reflect the ligand "bite," are very close to those in other Et_4dien complexes and, as would be expected, are also similar to those in ethylenediamine complexes.[27,50] However, unlike the ethylenediamine ligand, which is known to have both symmetrical and unsymmetrical *gauche* conformations,[50] the Et_4dien ligand has so far shown only the unsymmetrical form. The carbon atom displacements from the N–M–N plane are given in Table VII for each –N–C–C–N– unit of the Et_4dien ligand in three complexes.

The positions of the hydrogen atoms as obtained from least-squares refinement are chemically reasonable. The 28 methyl and methylene C–H distances have a mean value of 0.97 (36) Å. The single N–H distance is 0.97 (7) Å. The carbon–hydrogen and nitrogen–hydrogen bond distances and angles are given in Tables VIII and IX.

Thermal Vibrations.—The rms displacements along the principal axes of the temperature factor ellipsoids for the heavy atoms are given in Table X. Since no absorption correction was applied, no detailed analysis of thermal motion was made. In general, however, the ellipsoids are reasonable in size and orientation, varying from nearly spherical for Cu to highly elongated for N(3). The equatorial Br atom shows an anisotropy similar to that of the equatorial Br atoms in

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(43) I. E. Maxwell, *ibid.*, **10**, 1782 (1971).

(44) I. Agrell, *Acta Chem. Scand.*, **24**, 1247 (1970).

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(48) P. Gray and T. C. Waddington, *Trans. Faraday Soc.*, **53**, 901 (1957).

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TABLE VIII

C–H AND N–H BOND DISTANCES AND THEIR STANDARD DEVIATIONS[a]

Atoms	Distance, Å	Atoms	Distance, Å
C(1)–H(1)	0.81 (9)	C(7)–H(16)	0.95 (5)
C(1)–H(2)	0.86 (9)	C(8)–H(17)	0.96 (5)
C(1)–H(3)	1.08 (7)	C(8)–H(18)	1.18 (6)
C(2)–H(4)	1.12 (7)	C(9)–H(19)	1.08 (7)
C(2)–H(5)	0.82 (4)	C(9)–H(20)	0.80 (7)
C(3)–H(6)	1.07 (7)	C(9)–H(21)	0.96 (8)
C(3)–H(7)	0.90 (6)	C(10)–H(22)	0.92 (5)
C(4)–H(8)	0.94 (8)	C(10)–H(23)	0.95 (5)
C(4)–H(9)	0.92 (7)	C(11)–H(24)	1.00 (6)
C(4)–H(10)	0.90 (8)	C(11)–H(25)	1.07 (5)
C(5)–H(11)	0.98 (5)	C(12)–H(26)	0.83 (8)
C(5)–H(12)	1.06 (7)	C(12)–H(27)	1.15 (6)
C(6)–H(13)	0.96 (6)	C(12)–H(28)	0.96 (7)
C(6)–H(14)	0.94 (6)	N(5)–H(29)	0.95 (7)
C(7)–H(15)	1.12 (7)		

[a] See footnote *b*, Table III.

TABLE IX

BOND ANGLES AND STANDARD DEVIATIONS INVOLVING THE HYDROGEN ATOMS[a]

Atoms	Angle, deg	Atoms	Angle, deg
H(1)–C(1)–H(2)	120 (8)	H(15)–C(7)–N(5)	96 (3)
H(2)–C(1)–H(3)	90 (6)	H(16)–C(7)–C(8)	104 (4)
H(1)–C(1)–H(3)	110 (7)	H(17)–C(8)–H(18)	106 (3)
H(1)–C(1)–C(2)	116 (5)	H(17)–C(8)–C(7)	105 (3)
H(2)–C(1)–C(2)	107 (5)	H(18)–C(8)–N(6)	108 (6)
H(3)–C(1)–C(2)	110 (4)	H(19)–C(9)–H(20)	110 (6)
H(4)–C(2)–H(5)	108 (5)	H(20)–C(9)–H(21)	119 (6)
H(4)–C(2)–N(4)	104 (3)	H(19)–C(9)–H(21)	109 (6)
H(5)–C(2)–C(1)	111 (4)	H(19)–C(9)–C(10)	108 (4)
H(6)–C(3)–H(7)	107 (5)	H(20)–C(9)–C(10)	107 (5)
H(6)–C(3)–N(4)	110 (3)	H(21)–C(9)–C(10)	103 (4)
H(7)–C(3)–C(4)	117 (4)	H(22)–C(10)–H(23)	97 (5)
H(8)–C(4)–H(9)	113 (7)	H(22)–C(10)–C(9)	107 (4)
H(9)–C(4)–H(10)	106 (7)	H(23)–C(10)–N(6)	116 (3)
H(8)–C(4)–H(10)	98 (7)	H(24)–C(11)–H(25)	116 (4)
H(8)–C(4)–C(3)	114 (5)	H(24)–C(11)–N(6)	105 (3)
H(9)–C(4)–C(3)	115 (5)	H(25)–C(11)–C(12)	107 (3)
H(10)–C(4)–C(3)	110 (6)	H(26)–C(12)–H(27)	91 (6)
H(11)–C(5)–H(12)	104 (5)	H(26)–C(12)–H(28)	108 (7)
H(11)–C(5)–N(4)	112 (4)	H(26)–C(12)–C(11)	120 (5)
H(12)–C(5)–C(6)	103 (3)	H(27)–C(12)–C(11)	112 (4)
H(13)–C(6)–H(14)	104 (5)	H(28)–C(12)–C(11)	103 (4)
H(13)–C(6)–C(5)	111 (3)	H(29)–N(5)–C(6)	105 (4)
H(14)–C(6)–N(5)	112 (3)	H(29)–N(5)–C(7)	117 (3)

[a] See footnote *b*, Table III.

TABLE X

RMS DISPLACEMENTS (IN Å) ALONG THE PRINCIPAL AXES OF THE TEMPERATURE FACTOR ELLIPSOIDS

Atom	Min	Intermed	Max
Cu	0.193	0.202	0.228
Br	0.191	0.235	0.299
N(1)	0.200	0.236	0.294
N(2)	0.204	0.221	0.349
N(3)	0.222	0.288	0.589
N(4)	0.199	0.231	0.244
N(5)	0.185	0.212	0.257
N(6)	0.214	0.219	0.230
C(1)	0.231	0.273	0.425
C(2)	0.205	0.237	0.285
C(3)	0.205	0.297	0.313
C(4)	0.216	0.349	0.372
C(5)	0.197	0.232	0.306
C(6)	0.186	0.227	0.312
C(7)	0.195	0.252	0.270
C(8)	0.201	0.249	0.306
C(9)	0.208	0.303	0.354
C(10)	0.200	0.255	0.272
C(11)	0.227	0.244	0.303
C(12)	0.218	0.278	0.342

$CuBr_5^{3-}$,[34] with the angle between the maximum principal ellipsoid axis of the Br and the equatorial plane (plane B) being approximately the same as that found in $CuBr_5^{3-}$, 9.6 (8)°. Carbons 4 and 11, which have nonbonded contacts with the Br atom, have their strongest vibrations approximately perpendicular to the equatorial plane. The thermal ellipsoids of the nitrogens in the azido group are aligned such that the largest vibrations occur in the direction normal to the ligand internuclear axis.[51]

Crystal Packing.—The packing of the molecules in the crystal is shown in Figure 1 where the *a* and *c* axes are identified. The shortest contact is N(3)···H(18) [$x - 1, y, z$] equal to 2.47 Å. The only H···H contact less than 2.5 Å is H(11)···H(19) [$x, y, z + 1$] equal to 2.41 Å. The only intermolecular contact less than the sum of the appropriate van der Waals radii is the 3.36 Å value for N(3)···C(2) [$x - 1, y, z$].

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(51) We note two exceptions to this normal situation: see ref 43 and J. H. Enemark, *Inorg. Chem.*, **10**, 1952 (1971).