The Crystal Structure of $[Cu(N_3)_2(NH_3)_2]$

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The crystal structure of diazidodiaminecopper(II), $[Cu(N_3)_2(NH_3)_2]$,
has been determined by single crystal X-ray diffraction methods.
The elementary cell has the space group *Pnma* and contains four
formula units. The unit cell dimensions are $a = 6.389 \pm 0.005$ Å,
$b = 7.454 \pm 0.005$ Å and $c = 12.71 \pm 0.01$ Å, with $V = 605.3$ Å³.
The coordination around the copper atom is distorted octahedral,
there being four shorter and two longer copper-ligand bonds. The
octahedra are linked together to form chains by the sharing of corners.
The nitrogen-nitrogen distances in the azide groups have been deter-
mined to be 1.174 ± 0.011 Å, 1.142 ± 0.012 Å, and 1.186 ± 0.011 Å,
1.139 ± 0.013 Å, respectively.

The reliability index of the proposed structure is 0.075.

The infrared spectrum of $[Cu(N_3)_2(NH_3)_2]$ has also been registered.

Azide compounds were first investigated at the end of the 19th century,
when Curtius and Rissom [1] prepared several azides and examined their
explosive properties.

Dennis and Isham [2] prepared the first complex copper(II)-azides, *viz.*
$[Cu(N_3)_2(NH_3)_2]$ and $[Cu(N_3)_2(C_5H_5N)_2]$. Other additions compounds of copper
azide have also been described.[3] Dennis and Isham [2] formulated diazidodiamine-
copper(II) as $[Cu(NH_3)_2] (N_3)_2$ thus assuming that the azide groups exist as
anions. Straumanis and Cirulis [10] found, however, that the compound was not
an electrolyte and proposed the formula to be $[Cu(N_3)_2(NH_3)_2]$, which has been
verified by this investigation.

There are two distinctly different linear forms of the azide group. One is
the symmetric or ionic form in which the nitrogen-nitrogen distances are
equal and are 1.154 ± 0.015 Å.[4,5] The alkali metals, for instance, form such
ionic azides. The other form is asymmetric and the azide group and the atom
to which it is bonded are not collinear (see Fig. 1). To this group belong HN_3
and the organic azides, *e.g.* CH_3N_3 in which the N-N bond distances are 1.24
Å and 1.10 Å and the CH_3-N-N angle is $120 \pm 5°$.[6] These distances are in
close agreement with the distances calculated for the nitrogen-nitrogen double
(1.24 Å) and triple (1.10 Å) bonds.[7] Characteristic for most of these asym-
metric azides are their marked explosive properties.

$$\text{Na}^+ \; (\; \text{N} \; \underline{\overset{1.15\text{Å}}{\quad}} \; \text{N} \; \underline{\overset{1.15\text{Å}}{\quad}} \; \text{N} \;)^- \qquad (37)$$

Symmetric azide

$$\text{N} \; \underline{\overset{1.24\text{Å}}{\quad}} \; \text{N} \; \underline{\overset{1.10\text{Å}}{\quad}} \; \text{N} \qquad (6)$$

120°

Asymmetric azide

H₃C

Fig. 1.

The structures of, *e.g.*, CuN_3 [38] and AgN_3 [39] have been reported as having symmetrical azide groups, but there is a great difference between the crystal structures of, for instance, NaN_3 and CuN_3, the latter having chains of cuprous and azide ions and a Cu—N distance, which is shorter than the normal ion distance. This indicates a deviation from pure ionic bonding.

Besides the compound $[Cu(N_3)_2(NH_3)_2]$, investigated by the author, also reported earlier [8], there is an additional complex inorganic azide whose structure has recently been determined, namely $[CoN_3(NH_3)_5](N_3)_2$.[9] These two compounds are the only inorganic metal azides in which the presence of an asymmetric azide group has been ascertained.

Great attention has been paid to the explosive properties of copper(II)-azide and its addition compounds. It has been found that copper azide is very explosive.[1,10,40] None of the addition compounds of the copper azide, however, are explosive at normal pressure and temperatures.[3] Evans, Yoffe and Deb [11-13] suggest that the explosive properties of the simple metal azides are directly dependent on the ionisation potential of the metal to which the azide group is bonded.

Since there are very few crystal structure determinations of inorganic azides which have been carried out with sufficiently high precision to enable any conclusions to be drawn about the symmetry of the azide group, and as the azides are of technical importance, it is both of practical and theoretical interest that accurate structure determinations are performed. The present examination of the crystal structure of $[Cu(N_3)_2(NH_3)_2]$ provides a link in this investigation.

EXPERIMENTAL

Preparation. Severa different methods of preparation of $[Cu(N_3)_2(NH_3)_2]$ are described in the literature.[2,3,10,14] The author has used two different methods for the preparation of this compound, namely: (a) copper azide is precipitated from a solution of 2.5 g $CuSO_4 \cdot 5H_2O$ in 50 ml water by addition of a solution of 1.5 g NaN_3 in 15 ml water. The precipitate formed is dissolved in conc. NH_3. From this solution $[Cu(N_3)_2(NH_3)_2]$ crystallizes.[3] (b) 1.0 g $CuCl_2$ and 1.2 g KN_3 are dissolved in liq. NH_3 at about $-40°C$. Since KCl has a lower solubility in liq. NH_3 than KN_3, $CuCl_2$ and $Cu(N_3)_2$ [41-44] it is precipitated. The precipitate is filtered off and $[Cu(N_3)_2(NH_3)_4]$, probably, crystallizes from the filtrate. The crystals decompose in air forming $[Cu(N_3)_2(NH_3)_2]$ and NH_3. Recrystallization from conc. ammonia gives blue-green needle-shaped crystals, suitable for X-ray investigation.

The properties of the compound have been described elsewhere.[2,3,10]

Analysis. The amount of copper in $[Cu(N_3)_2(NH_3)_2]$ was determined by electrolysis.[15] The azide content was determined by titration with a Ce(IV)solution according to Arnold.[16] The ammonia content was determined by means of a Kjeldahl apparatus,[17] the ammonia being distilled into a solution of HCl and subsequently titrated with a NaOH solution. As the compound evolved ammonia in air, it is probable that a somewhat low value for the ammonia content was obtained. Found: Cu 34.9; N_3 47.1; NH_3 17.8. Calc.: Cu 35.0; N_3 46.3; NH_3 18.8).

STRUCTURE INVESTIGATION

X-Ray methods. The structural investigation was based on X-ray diffraction photographs of single crystals taken by the Weissenberg equi-inclination method.[18] Multiple film (4 films) photographs of nine zones were taken about two of the crystallographic axes, $CuK\alpha$ radiation being employed. The crystals were needle-shaped, the needle axis generally being parallel to the crystallographic *a*-axis.

The intensities of the reflexions obtained were estimated visually by comparison with a standard scale. The intensities were measured on all four films and an average value was calculated for every reflexion. The values obtained were corrected for Lorentz and polarisation effects. No correction was made for absorption, since μR was of the magnitude of 0.2.

The intensities of the different layer lines were brought to a common scale by comparison of the reflexions, occurring in more than one zone. The relative $|F_{obs}|$ values, which were obtained in this way, were compared with the later calculated structure factors and thus brought on to an absolute scale.

In order to obtain accurate values for the dimensions of the unit cell, X-ray powder photographs of $[Cu(N_3)_2(NH_3)_2]$ were taken in a Guinier focusing camera.[19] $CuK\alpha$ radiation was employed, and NaCl was used as an internal standard. A scale was copied on to the film before development in order to avoid the effect of uneven shrinkage of the film. The variation in the camera constant was determined by means of the NaCl lines.

Cell dimensions, space group and cell content. The elementary cell was found to have orthorhombic symmetry, and the lengths of its axes were determined to be [22] $a = 6.389 \pm 0.005$ Å, $b = 7.454 \pm 0.005$ Å, $c = 12.711 \pm 0.008$ Å, $V = 605.3$ Å³.

Calculated and observed $\sin^2 \theta$-values are given in Table 1.

From the X-ray photographs it was obvious that the following conditions of reflection were obeyed:

hkl: no conditions
0kl: $k + l = 2n$
h0l: no conditions
hk0: $h = 2n$

which are in accordance with the space groups $Pna2_1$ (No. 33) and $Pnma$ (No. 62).[7]

The density of diazidodiamminecopper(II) was determined to be 2.1 g/cm³. The unit cell thus contains four formula units ($\varrho_{calc} = 2.0$ g/cm³).

Table 1. X-Ray powder diffraction data for $[Cu(N_3)_2(NH_3)_2]$. Guinier camera. $CuK\alpha$ radiation.

h k l	$10^4\sin^2\theta_{obs}$	$10^4\sin^2\theta_{calc}$
0 1 1	142.8	143.7
1 1 1	288.8	289.3
1 0 2	293.0	292.7
0 2 0	427.8	427.8
2 0 0	581.8	582.4
1 1 3		583.5
0 0 4	588.2	588.5
1 2 2	720.3	720.5
2 1 1	727.1	726.1
1 0 4	733.4	734.1
2 1 2	837.0	836.4
1 1 4		841.0
0 3 1	1001.5	999.3
2 2 0	1010.0	1010.2
0 1 5	1028.0	1026.4
1 3 1	1143.7	1144.9
2 0 4	1172.2	1170.9
1 3 3	1437.6	1439.1
3 1 1 / 3 0 2	1455.6	1454.1 / 1457.5
1 0 6	1469.2	1469.7
2 3 1	1579.7	1581.7·
2 1 5	1610.8	1608.8
0 4 0	1710.9	1711.1
3 1 3	1749.9	1748.3
1 4 2 / 3 1 4	2005.0	2003.8 / 2005.8
1 1 7	2055.4	2054.8
2 3 5	2464.0	2464.4
3 3 3	2602.2	2603.9

Structure determination. The structure was assumed to be centrosymmetric and thus to belong to the space group *Pnma*. It was shown that a satisfactory description of the structure could be obtained based on this assumption.

Using the square of the $0kl$ structure factors a twodimensional Patterson summation was undertaken with the twodimensional Fourier programme 05—28,[20] the calculations being performed on Alwac III E. The largest peaks were obtained at ($\frac{1}{2}$, $\frac{1}{2}$), ($\frac{1}{2}$, 17/60), and (0, 13/60). Such peaks could be explained by placing Cu in the four-fold position (x, 0.250, 0.358). Using the signs of the structure factors obtained by placing copper in the above-mentioned position, an electron density projection on (100) was calculated with the 05—28 programme. From this projection it was then possible to obtain the y- and z-coordinates of most of the nitrogen atoms, and new structure factors could then be calculated using the programme KGK-1[21] and the computer Alwac III E. After several cycles all atoms, except the hydrogen atoms, were located in this projection. An approximate correction was made for the temperature factor using the factor exp $(-B \sin^2\theta\lambda^{-2})$,[23] where B is the temperature factor coefficient.

$R = \sum ||F_{obs}| - |F_{calc}||/\sum |F_{obs}|$ was calculated for $0kl$ and a value of $R_{0kl} = 0.11$ was obtained.

In order to determine the third coordinate of the atoms, a three-dimensional Patterson summation using the reflexions $0kl$-$1kl$, and a two-dimensional electron density projection on the plane (010) was used.

It was evident from the three-dimensional Patterson summation that the x-coordinate of the copper atom was approximately 0.250 and the copper atom was, therefore, assigned to the fourfold position (0.250, 0.250, 0.358). An electron density projection on (010) was calculated, using the signs of the structure factors, obtained by placing Cu in the above position. In this projection a false mirror plane appeared at $x = \frac{1}{4}$, while there was systematic extinction of the reflexions hkl with $k + l = 2n + 1$ owing to the allotted special position of the Cu atom in 0.250 The positions of several of the nitrogen atoms could, however, be elucidated from this projection. The signs of all structure factors were computed and a new electron density projection was obtained, in which the false mirror plane was eliminated, Cu being seen to lie not exactly in 0.250. The remaining nitrogen atoms were located by a difference synthesis ($F_{obs} - F_{calc}$). A correction was made for the temperature factor. After several cycles the value of $R_{h0l} = 0.17$ was obtained.

Refinement of the structure. The structure was refined using the "least-squares" method. A programme by Åsbrink and Brändén [24] was used and the calculations were performed on Facit EDB. The function $\sum w(|F_{obs}| - |F_{calc}|)^2$ was minimized, and the summation was made over all crystallographically independent planes. The weighting factor, w, was estimated by Cruickshank's weighting scheme.[24] A weighting analysis was calculated for every cycle of refinement in order to examine whether or not the used weighting scheme gave a good approximation.

In order to obtain a more rapid convergence, a fraction of the calculated shifts was applied, instead of the shifts themselves, following the method of Curtis.[24] The atomic scattering factors by Thomas und Umeda [25] for copper and by Freeman and Watson [26] for nitrogen were used as stated in *Intern. Tables*, Vol. III.[7]

Table 2. Atomic coordinates (expressed as fractions of the cell edges) and isotropic thermal parameters, B, with their standard deviations, δ, for [Cu(N₃)₂(NH₃)₂]. Space group *Pnma*. Four formula units in the unit cell. The numbers in parentheses after the atomic symbols have been used in order to distinguish the atoms (*cf.* Fig. 2).

Atom position		x	y	z	δ_x	δ_y	δ_z	B (Å²)	δ_B (Å²)
Cu(1)	4c	0.2264	0.2500	0.3595	0.0002		0.0001	3.28	0.02
N(2)	4c	0.3515	0.2500	0.2108	0.0014		0.0006	2.93	0.14
N(3)	4c	0.2315	0.2500	0.1408	0.0011		0.0005	2.20	0.12
N(4)	4c	0.1209	0.2500	0.0703	0.0016		0.0007	4.32	0.19
N(5)	4c	0.1200	0.2500	0.5119	0.0014		0.0006	3.23	0.15
N(6)	4c	0.2375	0.2500	0.5842	0.0012		0.0006	2.75	0.14
N(7)	4c	0.3445	0.2500	0.6559	0.0018		0.0007	4.07	0.19
N(8)	8d	0.2302	0.5162	0.3618	0.0009	0.0010	0.0004	3.06	0.10

Table 3. Observed and calculated structure factors for [Cu(N₃)₂(NH₃)₂].

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
0	2	0	148.4	-180.4	1	1	12	5.8	-5.1	2	0	6	41.4	-39.7	2	5	8	7.1	-7.0
0	4	0	144.7	151.6	1	1	13	14.7	12.9	2	0	8	46.0	-44.3	2	5	9	26.1	25.5
0	6	0	53.6	-61.5	1	1	15	6.6	6.7	2	0	9	16.7	-16.4	2	5	13	13.6	-13.1
0	8	0	32.2	42.1	1	2	1	3.3	3.8	2	0	10	39.6	37.3	2	6	1	5.4	6.2
0	0	2	14.9	-12.6	1	2	2	25.8	19.0	2	0	11	20.9	16.4	2	6	3	7.8	9.7
0	0	4	131.5	-135.8	1	2	3	6.2	5.9	2	0	12	13.8	11.5	2	6	4	26.4	-26.7
0	0	6	57.8	57.3	1	2	4	16.7	19.1	2	0	13	9.2	8.1	2	6	5	9.8	-10.8
0	0	8	53.8	51.5	1	2	5	19.0	17.3	2	0	14	31.8	-26.3	2	6	6	8.4	9.8
0	0	10	42.0	-40.9	1	2	6	34.4	32.7	2	1	0	32.1	-33.1	2	6	8	9.9	11.0
0	0	14	42.2	36.4	1	2	7	6.7	6.0	2	2	0	79.1	83.2	2	6	9	4.6	5.3
0	1	1	93.0	-98.7	1	2	8	25.6	-23.0	2	3	0	25.1	26.8	2	6	10	10.1	-11.2
0	3	3	27.7	26.7	1	2	9	11.2	11.1	2	4	0	91.4	-91.7	2	6	11	5.8	-7.1
0	4	4	78.0	-73.5	1	2	10	14.7	-12.6	2	5	0	11.6	-13.9	2	7	1	21.1	-23.2
0	5	5	33.7	32.8	1	2	12	12.3	10.7	2	6	0	34.1	36.9	2	7	2	5.3	7.6
0	6	6	16.3	-14.1	1	2	14	6.6	5.7	2	7	0	7.6	10.0	2	7	3	9.5	-10.0
0	8	8	13.3	12.1	1	3	1	60.3	-59.8	2	8	0	25.5	-28.7	2	7	4	5.2	-5.8
0	9	1	9.8	-10.9	1	3	2	11.7	-10.7	2	1	1	63.4	63.7	2	7	5	25.7	26.7
0	8	6	12.0	11.4	1	3	3	50.5	49.6	2	1	2	45.9	-43.7	2	7	8	4.1	5.6
0	8	4	23.4	-22.9	1	3	4	23.8	24.2	2	1	3	19.4	19.6	2	7	9	21.1	-20.9
0	7	5	28.8	-27.7	1	3	5	20.3	21.3	2	1	4	10.4	10.8	2	8	4	20.2	-22.0
0	6	2	26.2	29.4	1	3	6	7.5	7.9	2	1	5	77.2	-69.1	2	8	5	6.8	7.7
0	7	1	26.0	27.1	1	3	7	52.0	-54.8	2	1	8	13.3	-12.7	2	8	6	6.5	-8.5
0	4	2	11.0	-8.3	1	3	11	18.4	16.9	2	1	9	53.0	47.4	2	9	1	5.3	8.3
0	3	1	81.3	79.1	1	3	12	5.6	4.6	2	1	10	7.7	6.4	3	0	1	16.4	22.2
0	1	3	23.4	-26.5	1	3	13	13.5	-11.8	2	1	13	27.5	-22.8	3	0	2	66.3	-72.1
0	2	6	29.9	-28.2	1	3	15	6.5	-7.1	2	1	14	7.1	-5.5	3	0	3	17.3	-19.2
0	3	9	39.2	39.5	1	4	1	7.5	-6.9	2	1	15	8.8	7.8	3	0	4	25.2	26.7
0	4	14	32.3	26.4	1	4	2	39.1	37.4	2	2	1	13.1	15.1	3	0	5	7.4	5.4
0	5	13	22.4	19.2	1	4	4	24.0	-25.1	2	2	2	11.1	-11.7	3	0	6	34.6	36.0
0	1	15	10.8	-8.1	1	4	5	7.8	-9.0	2	2	3	27.7	27.0	3	0	7	15.5	15.8
0	2	14	29.2	-23.9	1	4	6	47.6	-48.0	2	2	4	57.5	-54.7	3	0	8	33.5	-33.0
0	3	13	35.9	-30.6	1	4	7	7.9	-7.2	2	2	5	25.5	-23.5	3	0	9	9.6	11.0
0	7	9	20.2	19.6	1	4	8	30.8	30.1	2	2	6	18.8	18.3	3	0	10	24.4	-22.3
0	1	13	38.8	33.3	1	4	9	7.0	-7.9	2	2	8	21.9	19.7	3	0	11	11.8	-10.5
0	4	10	28.4	-27.6	1	4	10	20.7	19.6	2	2	9	10.7	9.4	3	0	12	24.0	19.8
0	5	9	22.8	-22.3	1	4	12	18.2	-17.4	2	2	10	22.8	-20.5	3	0	14	5.0	4.9
0	6	8	14.3	-12.4	1	4	14	7.1	-7.6	2	2	11	17.5	-14.3	3	0	15	7.4	6.2
0	2	10	24.5	21.0	1	5	1	25.6	28.7	2	2	13	5.8	-4.8	3	1	1	33.7	-37.7
0	4	8	36.4	33.4	1	5	2	6.1	5.4	2	2	14	20.1	15.8	3	1	2	25.8	-28.7
0	1	9	46.1	-41.6	1	5	3	21.5	-22.9	2	3	1	56.7	-56.3	3	1	3	42.6	44.2
0	2	8	23.0	-21.4	1	5	4	10.6	-12.9	2	3	2	24.8	28.4	3	1	4	33.7	32.4
0	4	6	34.7	34.3	1	5	5	11.3	-10.8	2	3	3	20.3	-21.1	3	1	5	28.7	26.5
0	3	5	62.4	-62.1	1	5	7	28.4	28.8	2	3	4	10.4	-11.4	3	1	6	14.4	13.7
0	1	5	66.2	66.8	1	5	11	8.4	-7.3	2	3	5	64.6	61.3	3	1	7	10.3	-11.8
0	2	4	49.4	54.8	1	5	13	8.6	7.5	2	3	8	10.7	11.4	3	1	8	12.5	-9.7
1	0	2	60.7	58.7	1	6	2	9.4	-6.1	2	3	9	47.0	-43.2	3	1	10	8.4	-8.4
1	0	4	38.6	-44.8	1	6	4	9.6	9.5	2	3	10	6.0	-6.2	3	1	11	18.7	15.3
1	0	5	20.7	-18.7	1	6	6	17.0	17.1	2	3	13	25.1	21.5	3	1	12	11.6	9.5
1	0	6	78.8	-80.2	1	6	8	12.0	-12.3	2	3	14	6.1	5.0	3	1	13	9.1	-7.6
1	0	7	11.0	-11.9	1	6	10	6.9	-6.6	2	4	1	14.5	-16.7	3	1	15	9.6	-6.9
1	0	8	45.4	46.3	1	6	12	6.3	5.8	2	4	2	12.1	13.8	3	2	1	9.2	-9.3
1	0	9	14.5	-12.9	1	7	1	21.8	-22.2	2	4	3	18.1	-20.9	3	2	2	23.5	23.9
1	0	10	31.5	29.5	1	7	3	20.4	20.5	2	4	4	69.3	66.6	3	2	4	11.4	-12.7
1	0	12	26.0	-24.9	1	7	4	5.7	7.1	2	4	5	23.7	22.7	3	2	5	9.2	-8.6
1	0	14	11.1	-10.5	1	7	5	9.6	9.4	2	4	6	25.4	-25.0	3	2	6	10.0	-9.0
1	0	16	9.7	8.7	1	7	7	20.7	-22.9	2	4	8	30.9	-29.2	3	2	8	18.0	17.4
1	1	1	66.2	73.9	1	8	2	13.6	13.0	2	4	9	11.3	-11.3	3	2	10	11.9	10.3
1	1	2	12.2	12.3	1	8	4	6.9	-7.7	2	4	10	26.5	25.8	3	2	12	11.7	-8.9
1	1	3	46.8	-51.6	1	8	6	14.2	-15.4	2	4	11	11.9	11.3	3	3	1	31.7	34.3
1	1	4	34.4	-35.2	1	8	8	9.3	10.6	2	4	12	8.6	8.1	3	3	2	24.4	25.3
1	1	5	20.8	-23.1	1	9	1	6.7	7.5	2	4	13	5.4	5.8	3	3	3	41.4	-41.2
1	1	6	9.9	-9.4	1	9	3	5.6	-5.2	2	4	14	20.7	-19.2	3	3	4	26.2	-25.1
1	1	7	87.7	61.6	2	0	1	30.0	-32.0	2	5	1	26.9	28.5	3	3	6	13.5	-12.8
1	1	8	4.9	3.1	2	0	2	22.9	24.9	2	5	2	12.1	-15.4	3	3	7	14.6	14.7
1	1	9	5.8	-5.0	2	0	3	41.2	-40.7	2	5	3	8.8	9.8	3	3	8	9.9	8.8
1	1	10	5.6	4.7	2	0	4	115.5	114.8	2	5	4	6.8	6.1	3	3	11	18.0	-15.1
1	1	11	17.9	-16.4	2	0	5	37.6	38.4	2	5	5	32.8	-33.4					

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
3	3	12	10.0 -	8.7	3	0	4	26.2	26.7	2	1	5	75.8 -	69.1	2	2	1	13.2	15.1
3	3	13	7.1	6.9	3	0	5	6.9	5.4	2	1	8	12.1 -	12.7	2	2	2	10.4 -	11.7
3	4	1	14.6	14.2	3	0	6	35.7	36.0	2	1	9	48.6	47.4	2	2	3	29.0	27.0
3	4	2	45.4 -	43.4	3	0	7	15.8	15.8	2	1	10	7.3	6.4	2	2	4	62.4 -	54.7
3	4	3	14.2 -	13.1	3	0	8	32.3 -	33.0	2	1	13	23.9 -	23.8	2	2	5	24.8 -	23.5
3	4	4	18.0	17.1	3	0	9	8.5	11.0	2	1	14	6.2 -	5.5	2	2	6	17.7	18.3
3	4	6	25.2	23.7	3	0	10	22.0 -	22.3	2	1	15	7.8	7.8	2	2	8	20.8	19.7
3	4	7	10.7	10.5	3	0	12	22.5	19.8	3	1	1	43.5 -	37.7	2	2	9	10.1	9.4
3	4	8	23.1 -	22.2	3	0	11	11.1 -	10.5	3	1	2	27.4 -	28.7	2	2	10	22.7 -	20.5
3	4	10	17.2 -	15.6	3	0	15	5.8	6.2	3	1	3	46.3	44.3	2	2	11	15.1 -	14.3
3	4	11	8.2 -	7.3	4	0	1	29.4	30.8	3	1	4	35.5	32.4	2	2	14	17.7	15.8
3	4	12	15.9	13.7	4	0	2	12.7 -	12.9	3	1	5	28.5	26.5	3	2	1	9.0 -	9.3
3	5	1	17.4 -	17.3	4	0	3	17.9	20.3	3	1	6	13.3	13.7	3	2	2	24.6	23.9
3	5	2	13.5 -	13.6	4	0	4	67.6 -	64.6	3	1	7	8.7 -	11.8	3	2	4	10.5 -	12.7
3	5	3	20.3	21.1	4	0	5	39.4 -	38.9	3	1	8	10.5 -	9.7	3	2	5	8.0 -	8.6
3	5	4	12.2	14.8	4	0	6	15.0	16.5	3	1	10	7.3 -	8.4	3	2	6	8.5 -	9.0
3	5	5	12.3	12.5	4	0	8	27.1	27.6	3	1	11	17.2	15.3	3	2	8	16.2	17.4
3	5	11	8.8	7.3	4	0	9	26.1	26.3	3	1	12	10.0	9.5	3	2	9	8.0 -	9.6
3	6	2	13.1	13.4	4	0	10	24.2 -	24.7	3	1	13	7.0 -	7.6	3	2	10	11.3	10.3
3	7	7	9.1	7.8	4	0	12	8.4 -	7.9	4	1	1	28.2 -	28.9	3	2	12	9.4 -	8.9
3	7	1	14.0	14.4	4	0	13	9.0 -	9.4	4	1	3	13.5 -	15.0	4	2	1	14.9 -	16.2
3	7	2	9.3	10.4	4	0	14	11.1	12.5	4	1	4	26.2 -	27.1	4	2	3	10.4 -	11.2
3	7	3	17.8 -	18.0	5	0	1	19.1 -	19.2	4	1	5	48.4	49.6	4	2	4	40.5	36.1
3	7	5	7.7 -	9.5	5	0	2	31.6	36.4	4	1	6	8.4	8.2	4	2	5	26.2	24.3
3	8	2	12.8 -	13.3	5	0	3	28.2	26.6	4	1	8	12.4	13.8	4	2	8	13.4 -	13.4
3	8	4	6.1	6.1	5	0	4	16.2 -	18.9	4	1	9	38.9 -	38.1	4	2	9	16.7 -	17.0
3	8	6	6.8	7.8	5	0	5	13.3	15.0	4	1	10	13.0 -	11.8	4	2	10	12.5	14.4
3	2	7	6.3 -	5.4	5	0	6	11.3 -	15.5	4	1	13	8.4	9.6	5	2	1	7.8	9.3
3	2	9	9.1 -	9.6	5	0	7	10.1 -	13.3	5	1	1	14.8	16.4	5	2	2	15.6 -	16.1
3	5	6	7.0	6.5	5	0	8	14.2	16.4	5	1	2	20.3	22.5	5	2	3	13.2 -	14.2
3	5	7	6.9 -	5.4	5	0	10	14.5	12.7	5	1	3	16.8 -	19.4	5	2	4	9.6	12.2
3	5	12	4.5	5.3	5	0	11	12.6	11.7	5	1	5	8.4 -	9.3	5	2	5	8.0 -	9.9
3	6	4	6.9 -	7.1	5	0	12	11.8 -	11.4	5	1	6	9.2 -	11.2	5	2	8	6.4 -	8.5
3	6	6	6.7 -	6.0	6	0	1	23.1 -	22.8	5	1	8	11.4	11.9	5	2	10	5.4 -	6.1
3	6	8	8.5	9.1	6	0	4	23.8	23.8	5	1	10	5.2	6.5	5	2	11	5.0 -	5.6
3	6	10	5.0	5.9	6	0	5	26.6	24.1	5	1	11	6.9 -	7.6	5	2	12	3.9	5.1
3	7	4	7.4 -	9.3	6	0	8	13.1 -	12.6	5	1	12	6.2 -	6.6	6	2	1	11.5	13.3
3	8	1	5.2	5.1	6	0	9	18.3 -	19.9	6	1	1	10.9	13.1	6	2	4	11.0 -	12.7
3	8	3	5.0 -	4.6	6	0	10	8.2	10.2	6	1	2	11.3	11.8	6	2	5	12.9 -	14.2
2	0	0	196.2 -	172.6	7	0	1	10.6	12.7	6	1	3	6.6	8.4	6	2	9	11.2	12.5
4	0	0	40.4	47.3	7	0	3	15.5 -	15.9	6	1	4	22.0	22.9	7	2	3	6.8	8.1
6	0	0	25.3 -	26.3	7	0	5	8.3 -	9.8	6	1	5	18.4 -	21.1	7	2	7	4.5 -	6.5
8	0	0	15.6	14.2	7	0	6	6.5	8.2	6	1	6	7.3 -	8.7	0	2	2	52.8	54.8
1	0	1	12.2 -	11.6	7	0	7	15.9	13.3	6	1	9	13.7	15.6	0	2	6	30.9 -	28.2
1	0	2	68.5	58.7	8	0	1	14.4	13.5	6	1	10	9.5	10.1	0	2	8	22.3 -	21.4
1	0	4	43.9 -	44.8	0	0	2	12.3 -	12.6	7	1	1	4.8 -	6.9	0	2	10	22.0	21.0
1	0	5	21.6 -	18.7	0	0	4	138.6 -	135.8	7	1	2	6.7 -	9.3	0	2	14	27.8 -	23.9
1	0	6	86.2 -	80.2	0	0	6	52.5	57.3	7	1	6	7.0	9.3	2	3	0	28.1	26.8
1	0	7	11.1 -	11.5	0	0	8	50.2	51.5	7	1	7	3.5 -	4.2	4	3	0	23.6 -	21.9
1	0	8	45.0	46.3	0	0	10	39.8 -	40.9	7	1	8	7.3 -	7.9	6	3	0	22.4	21.4
1	0	9	13.3 -	12.9	0	0	12	9.4 -	10.6	0	1	3	25.0 -	26.5	1	3	1	62.0 -	59.8
1	0	10	31.0	29.5	0	0	14	39.5	36.4	0	1	5	73.5	66.8	1	3	2	11.4 -	10.7
1	0	12	24.7 -	24.9	2	1	0	35.7 -	33.1	0	1	7	10.9	9.5	1	3	3	56.9	49.6
1	0	14	11.4 -	10.5	4	1	0	21.2	22.9	0	1	9	47.2 -	41.6	1	3	4	23.0	24.2
1	0	16	8.7	8.7	6	1	0	18.7 -	22.9	0	1	11	7.3	7.2	1	3	5	21.8	21.3
2	0	1	35.1 -	32.0	8	1	0	16.8	18.7	0	1	13	40.8	33.3	1	3	6	6.7	7.9
2	0	2	27.2	24.9	1	1	1	75.4	72.9	0	1	15	7.3 -	8.1	1	3	7	56.0 -	54.8
2	0	3	42.5 -	40.7	1	1	2	11.0	12.2	2	2	0	84.8	83.2	1	3	11	16.6	16.9
2	0	4	117.6	114.8	1	1	3	54.1 -	51.6	2	2	0	14.7 -	15.4	1	3	13	10.7 -	11.6
2	0	5	40.2	38.4	1	1	4	40.0 -	35.2	6	2	0	12.1	13.2	1	3	15	5.2 -	7.1
2	0	6	40.4 -	39.7	1	1	5	21.7 -	23.1	1	2	2	29.0	19.0	2	3	2	56.8 -	56.3
2	0	8	49.5 -	44.3	1	1	7	72.2	61.6	1	2	3	4.9	5.9	2	3	3	20.2 -	21.1
2	0	9	14.5 -	16.4	1	1	11	17.2 -	16.4	1	2	4	17.5	19.1	2	3	3	11.0 -	11.4
2	0	10	36.6	37.3	1	1	13	13.3	12.9	1	2	5	18.4	17.3	2	3	5	66.7	61.4
2	0	11	18.8	16.4	1	1	15	6.4	6.7	1	2	6	35.1	32.7	2	3	8	9.5	11.4
2	0	12	13.1	11.5	1	1	6	9.8 -	9.4	1	2	7	7.0	6.0	2	3	9	45.5 -	43.2
2	0	14	26.9 -	26.3	2	1	1	65.8	63.7	1	2	8	24.1 -	23.0	2	3	13	23.6	21.5
3	0	1	23.5	22.2	2	1	2	49.7 -	43.7	1	2	9	10.6	11.1	2	3	14	5.0	5.0
3	0	2	70.3 -	72.1	2	1	3	18.3	19.6	1	2	10	13.1 -	12.6	3	3	1	34.7	34.3
3	0	3	19.8 -	19.2	2	1	4	9.5	10.8	1	2	12	11.2	10.7					

h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc	h	k	l	|Fo|	Fc
3	3	2	25.0	25.3	6	3	3	7.8	- 8.1	1	4	12	19.3	- 17.4	4	4	5	27.0	- 25.8
3	3	3	44.4	- 41.2	6	3	4	24.3	- 21.0	1	4	14	6.5	- 7.6	4	4	6	10.2	11.3
3	3	4	27.2	- 25.1	6	3	5	20.8	19.5	2	4	1	14.7	- 16.7	4	4	8	19.6	19.1
3	3	5	23.4	- 22.6	6	3	6	8.6	8.0	2	4	2	12.5	13.8	4	4	9	20.1	18.7
3	3	6	11.6	- 12.8	6	3	8	9.1	8.8	2	4	3	18.9	- 20.9	4	4	10	17.5	- 17.9
3	3	7	13.7	14.7	6	3	9	15.8	- 14.7	2	4	4	70.0	66.6	4	4	11	3.7	- 4.6
3	3	8	9.5	8.8	7	3	2	8.1	9.2	2	4	5	23.3	22.7	4	4	12	4.9	- 5.5
3	3	11	15.9	- 15.1	7	3	6	8.8	- 9.0	2	4	6	24.2	- 25.0	5	4	1	13.2	- 12.8
3	3	12	8.8	- 8.7	0	3	1	68.9	79.1	2	4	8	31.3	- 29.2	5	4	2	24.2	24.0
3	3	13	7.0	6.9	0	3	3	27.5	26.7	2	4	9	11.5	- 11.3	5	4	3	19.7	18.2
4	3	1	25.2	27.4	0	3	5	59.2	- 62.1	2	4	10	25.2	25.8	5	4	4	11.9	- 13.0
4	3	3	14.4	14.9	0	3	7	8.5	- 8.6	2	4	11	11.2	11.3	5	4	5	9.0	10.2
4	3	4	26.0	24.4	0	3	9	34.9	39.5	2	4	12	7.6	8.1	5	4	6	10.4	- 10.5
4	3	5	44.7	- 44.0	0	3	11	5.3	- 6.4	2	4	13	4.5	5.8	5	4	7	9.1	- 9.2
4	3	6	8.3	- 7.9	0	3	13	34.6	- 30.6	2	4	14	18.2	- 19.2	5	4	8	11.9	11.4
4	3	8	11.4	- 12.8	0	3	15	5.8	7.7	3	4	1	16.0	14.2	5	4	10	9.6	9.2
4	3	9	33.1	34.7	2	4	0	89.9	- 91.7	3	4	2	46.0	- 43.4	6	4	1	16.4	- 16.3
4	3	10	11.7	10.9	4	4	0	32.1	32.0	3	4	3	15.2	- 13.0	6	4	4	17.9	17.2
4	3	13	7.1	- 9.6	6	4	0	17.6	- 18.8	3	4	4	17.6	17.1	6	4	5	18.3	17.3
5	3	1	14.8	- 15.7	1	4	1	6.5	- 6.9	3	4	6	27.9	23.7	6	4	8	8.3	- 9.2
5	3	2	21.6	- 20.7	1	4	2	37.1	37.4	3	4	7	10.0	10.5	7	4	1	8.0	9.0
5	3	3	18.8	18.8	1	4	4	24.8	- 25.1	3	4	8	22.9	- 22.2	7	4	3	9.7	- 11.2
5	3	5	8.3	8.6	1	4	6	53.1	- 48.0	3	4	10	17.5	- 15.6	7	4	4	3.6	6.3
5	3	6	10.3	11.0	1	4	5	7.5	- 9.0	3	4	11	7.0	- 7.3	0	4	4	74.6	- 73.5
5	3	8	12.3	- 10.9	1	4	7	6.8	- 7.2	3	4	12	15.6	13.7	0	4	6	33.2	34.3
5	3	11	7.8	7.7	1	4	8	29.1	30.1	4	4	1	20.4	19.8	0	4	8	33.0	-33.4
6	3	1	11.4	- 12.5	1	4	9	6.3	- 7.9	4	4	2	7.2	- 8.0	0	4	10	26.5	- 27.6
6	3	2	11.4	- 10.2	1	4	10	20.2	19.6	4	4	3	11.1	13.2	0	4	12	6.3	- 7.6
										4	4	4	44.7	- 42.6	0	4	14	26.9	26.4

The refinement was performed with the complete reflexion material (about 700 reflexions). It was terminated when the shifts of the atomic coordinates had become less than 1/10 of the standard deviation. The reliability factor R for all observed reflexions was then 0.075. The atomic coordinates are to be found in Table 2, and observed and calculated structure factors in Table 3.
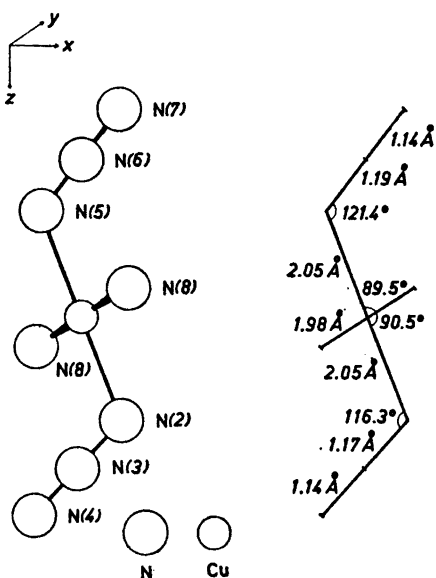
Fig. 2. A formula unit of $[Cu(N_3)_2(NH_3)_2]$. N(2), N(3), N(4), and N(5), N(6), N(7), respectively, form the two azide groups. N(8) is the nitrogen in the ammine group.

DESCRIPTION OF THE STRUCTURE

The structure of one formula unit of the compound $[Cu(N_3)_2(NH_3)_2]$ is reproduced in Fig. 2. Bond lengths and bond angles within this unit are to be found in Table 4. Fig. 3a shows a projection along the b-axis and Fig. 3b an

Table 4. Bond distances and angles, with their standard deviations, δ, in a formula unit of $[Cu(N_3)_2(NH_3)_2]$.

	Distance (Å)	δ (Å)		Angle (°)	δ (°)
Cu(1)—N(2)	2.052	0.008	N(2)—Cu(1)—N(8)	90.5	0.5
Cu(1)—N(5)	2.053	0.008	N(5)—Cu(1)—N(8)	89.5	0.5
Cu(1)—N(8)	1.985	0.008	Cu(1)—N(2)—N(3)	116.3	0.5
N(2)—N(3)	1.174	0.011	Cu(1)—N(5)—N(6)	121.4	0.5
N(3)—N(4)	1.142	0.012	N(2)— N(3)—N(4)	177.5	0.7
N(5)—N(6)	1.186	0.011	N(5)— N(6)—N(7)	177.6	0.7
N(6)—N(7)	1.139	0.013			
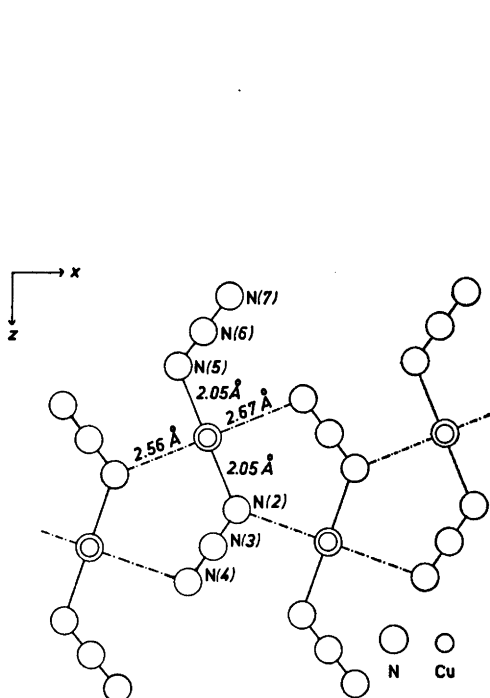
Fig. 3a. Projection of the structure along the b-axis. The longer bond distances in the octahedra are denoted by ·—·—·—·. The ammine groups (N(8)) are placed above and below the Cu atom.
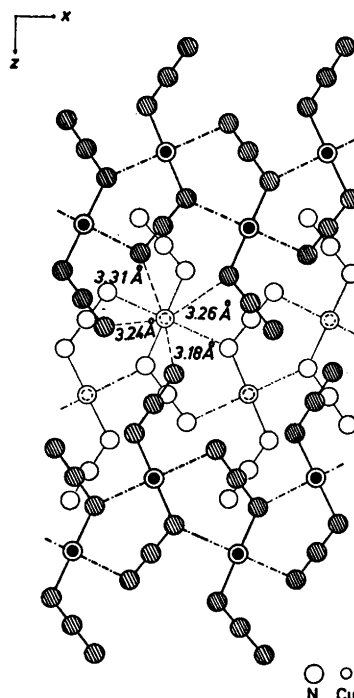
Fig. 3b. Extension of the projection along the b-axis. The shaded (azide groups) and the black (Cu) atoms are in the same plane. The atoms marked with fine lines belong to a chain in a plane below. Possible hydrogen bond distances are denoted by — — — — —.

extension of this projection including possible hydrogen bonds. Figs. 4 and 5 illustrate from two different points of view, how the structure is built up by the linking of somewhat distorted octahedra. Atomic distances and angles within and between the chains are given in Tables 5 and 6.
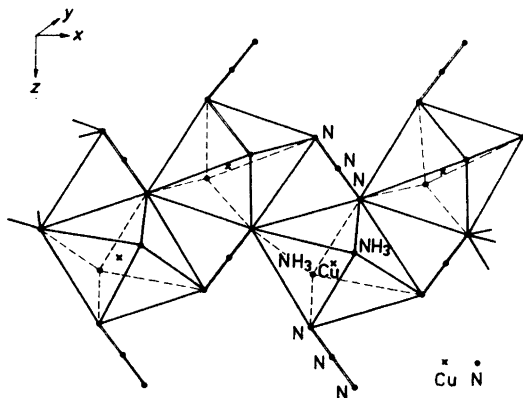
Fig. 4. The chains of octahedra from which the structure is built up, as viewed perpendicular to the *xz*-plane.

The copper atom is surrounded by four nitrogen atoms in an almost square-planar configuration, two of the nitrogen atoms coming from an ammine group and the remaining two being end nitrogen atoms in an azide group. The distance from the central copper atom to the nitrogen atom in the ammine group has been determined to be 1.985 ± 0.008 Å, and, owing to symmetry reasons, both $Cu-NH_3$ bond lengths must be equal. The $Cu-N_3$ distances have been calculated as being 2.053 ± 0.008 Å and 2.052 ± 0.008 Å. The angles between copper-ligand bonds have been found within experimental error to be 90° (90.5 ± 0.5° and 89.5 ± 0.5°). Besides these four nearest neighbours the copper atom has two other neighbouring nitrogen atoms at distances 2.56 ± 0.01 Å and 2.67 ± 0.01 Å (Fig. 3a). These form, together with the four nitrogen atoms mentioned earlier, an octahedron which is somewhat distorted in one direction.

The structure can thus be visualised as being built up of octahedra, linked together through a common corner as well as through an azide group, to form chains (Figs. 4 and 5). These chains, in their turn, may be joined together by hydrogen bonding, in which the hydrogen atoms are bonded to the nitrogen atoms of the azide groups in adjacent chains. The distances, from the nitrogen atom in an ammine group to the nitrogen atoms to which hydrogen bonding might occur, as calculated from the atomic coordinates, are 3.18 Å, 3.24 Å, 3.26 Å, and 3.31 Å ± 0.01 Å (Tab. 5, Fig. 3b).

The nitrogen-nitrogen distances within the azide groups $N(2)-N(3)-N(4)$ (nomenclature see Table 2 and Fig. 2) have been determined to be 1.174 ± 0.011 Å and 1.142 ± 0.012 Å, with the longest distance closest to the $Cu-N$

Table 5. Atomic distances in $[Cu(N_3)_2(NH_3)_2]$ other than bond distances within the formula unit. The numbers between the square brackets indicate the number of unit cell translations in the x-, y-, and z-directions, and the number directly following indicates the symmetry operation performed, according to *International Tables*, Vol. I.[7]

	Distance (Å)	δ (Å)
Within the chain		
Cu(1) [0 0 0] 1 — Cu(1) [0 0 0] 4	4.238	0.004
Cu(1) [0 0 0] 1 — N(2) [−1 0 0] 4	2.56	0.01
Cu(1) [0 0 0] 1 — N(4) [0 0 0] 4	2.67	0.01
Cu(1) [0 0 0] 1 — N(3) [0 0 0] 1	2.78	0.01
Cu(1) [0 0 0] 1 — N(4) [0 0 0] 1	3.74	0.01
Cu(1) [0 0 0] 1 — N(6) [0 0 0] 1	2.86	0.01
Cu(1) [0 0 0] 1 — N(7) [0 0 0] 1	3.84	0.01
N(2) [0 0 0] 1 — N(4) [0 0 0] 1	2.32	0.02
N(2) [0 0 0] 1 — N(2) [0 0 0] 4	3.35	0.02
N(2) [0 0 0] 1 — N(4) [0 0 0] 4	3.27	0.02
N(2) [0 0 0] 1 — N(5) [0 0 0] 1	4.10	0.02
N(2) [0 0 0] 1 — N(5) [0 0 0] 4	3.31	0.02
N(4) [0 0 0] 1 — N(5) [0 0 0] 4	3.36	0.02
N(4) [0 0 0] 1 — N(5) [−1 0 0] 4	3.37	0.02
N(4) [0 0 0] 1 — N(7) [−1 0 0] 4	3.37	0.02
N(5) [0 0 0] 1 — N(7) [0 0 0] 1	2.33	0.02
N(2) [0 0 0] 1 — N(8) [0 0 0] 1	2.87	0.01
N(2) [0 0 0] 1 — N(8) [0 0 0] 2	3.26	0.01 ·
N(4) [0 0 0] 1 — N(8) [−1 0 0] 2	3.30	0.01
N(5) [0 0 0] 1 — N(8) [0 0 0] 1	2.84	0.01
Between the chains		
N(4) [0 0 0] 1 — N(8) [0 1 −1] 4	3.31	0.01
N(5) [0 0 0] 1 — N(8) [0 −1 1] 3	3.26	0.01
N(7) [0 0 0] 1 — N(8) [1 −1 1] 3	3.24	0.01
N(7) [0 0 0] 1 — N(8) [0 1 0] 4	3.18	0.01
N(7) [0 0 0] 1 — N(7) [0 0 1] 4	3.99	0.02
Cu(1) [0 0 0] 1 — N(7) [0 0 −1] 3	4.56	0.02
N(3) [0 0 0] 1 — N(7) [0 0 −1] 3	3.76	0.02
N(8) [0 0 0] 1 — N(8) [0 1 1] 5	4.59	0.02

Table 6. Angles in $[Cu(N_3)_2(NH_3)_2]$ other than bond angles within the formula unit. Notations as in Table 5.

	angle (°)	δ (°)
N(2) [0 0 0] 1 — Cu(1) [0 0 0] 1 — N(4) [0 0 0] 4	86.6	0.4
N(2) [0 0 0] 1 — Cu(1) [0 0 0] 1 — N(2) [−1 0 0] 4	92.5	0.5
N(2) [−1 0 0] 4 — Cu(1) [0 0 0] 1 — N(5) [0 0 0] 1	91.1	0.5
N(4) [0 0 0] 4 — Cu(1) [0 0 0] 1 — N(5) [0 0 0] 1	89.8	0.5
Cu(1) [0 0 0] 1 — N(2) [0 0 0] 1 — Cu(1) [0 0 0] 4	133.4	0.4
N(2) [0 0 0] 1 — Cu(1) [0 0 0] 1 — N(3) [0 0 0] 1	22.3	0.5
N(3) [0 0 0] 1 — Cu(1) [0 0 0] 1 — N(6) [0 0 0] 1	177.9	0.4
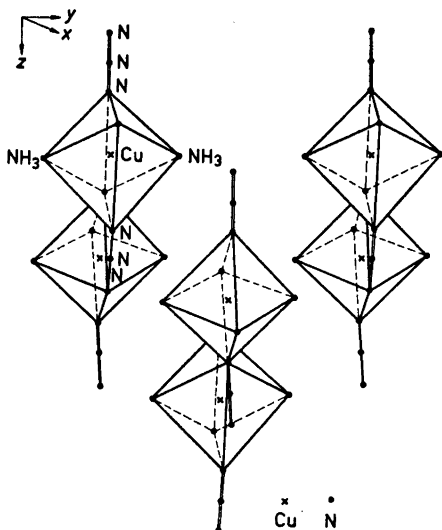
Fig. 5. The packing of the chains of octa-
hedra as viewed perpendicular to the *yz*-
plane.

bonding. The difference between these bond lengths is not quite statistically
significant. The axis of the azide group makes an angle of 116.3 $\pm$ 0.5° with
the Cu—N bond. In the other azide group, N(5)—N(6)—N(7), the nitrogen-
nitrogen distances have been determined to be 1.186 $\pm$ 0.011 Å and 1.139
$\pm$ 0.013 Å, these bond lengths being significantly different. The angle between
the azide group and the Cu-N bond is in this case 121.4 $\pm$ 0.5.°

IR-SPECTRUM OF DIAZIDODIAMMINECOPPER(II)

The IR-spectrum was registered by a "Perkin-Elmer 337 Grating Infrared
Spectrophotometer". The sample was powdered and the potassium bromide
technique was used. The spectrum is shown in Fig. 6.
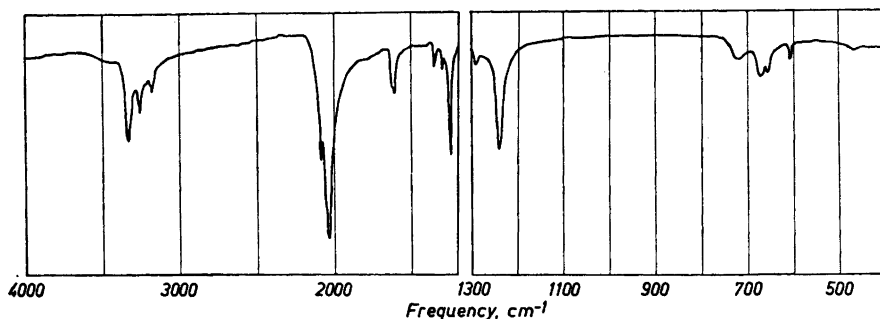
Fig. 6. Infrared spectrum of $[Cu(N_3)_2(NH_3)_2]$.

The strong bands at 2040 cm^{-1} and 2080 cm^{-1} may be accounted for by the antisymmetric stretching frequency of the azide group.[27-30] According to Nakamoto [29] the complexes [Cr(N$_3$)$_3$(NH$_3$)$_3$] and [Co(N$_3$)$_3$(NH$_3$)$_3$] show corresponding stretching frequencies at 2072 cm^{-1} and 2017 cm^{-1}, respectively. Chemical properties indicate that the Cr(III) complex is more strongly covalent than the Co(III) complex, which should imply that the difference in the nitrogen-nitrogen distances in the Cr-complex is larger than in the Co-complex. Thus, as the nitrogen-nitrogen distances approach one another the frequency should be lowered; this property is also reported by other authors.[27,30] In [Cu(N$_3$)$_2$(NH$_3$)$_2$] there are two azide groups, with different nitrogen-nitrogen distances (1.17 Å and 1.14 Å, 1.19 Å and 1.14 Å, respectively). Despite the statistical nonsignificance of the difference between these two azide groups, the observed splitting into two bands is indicative of such a difference, and the band at 2040 cm^{-1} might accordingly originate from the azide group with bond lengths 1.17 Å and 1.14 Å, while the band at 2080 cm^{-1} could be due to the group with bond lengths 1.19 Å and 1.14 Å.

The azide group also has a symmetric vibration frequency, between 1340 cm^{-1} and 1180 cm^{-1},[27] this is, however, much weaker than the antisymmetric stretching frequency, and since the ammine groups also show absorption in this region, it is more difficult to locate. The smaller peaks observed for [Cu(N$_3$)$_2$(NH$_3$)$_2$] at 1290 cm^{-1} and 1340 cm^{-1} probably originate from this vibration.

The spectrum also shows three peaks, close to each other, at the frequencies 3340 cm^{-1}, 3260 cm^{-1}, and 3180 cm^{-1}, which most probably originate from N—H stretchings. A pure N—H bond has, according to Brügel,[31] an absorption band at 3400 cm^{-1}. The displacement of the peaks to lower frequencies indicates the presence of hydrogen bonding (N—H···N). There is a relation between the displacement of the frequency and the distance between the nitrogen atoms.[32] Pimentel and Sederholm have given an equation for this relation.[33] Nakamoto et al.[34] also give a linear relation between the bonding distances of the nitrogen atoms and the frequency of the absorption peak. These different relations give different results, but neither of them is sufficiently supported by experiment to be considered reliable.

The spectrum also shows other bands, e.g. the peak at 1240 cm^{-1}, which are supposed to originate from the ammine ligands. The regions in which these peaks are found are in good agreement with the investigations of Nakamoto,[29] who has examined a number of ammine complexes.

DISCUSSION

The distances between the copper atom and the nitrogen atoms have been determined to be 1.985 Å in the ammine groups and to be 2.053 Å and 2.052 Å in the azide groups (Table 4). These distances are in good agreement with the Cu—N distances, reported in other structures, see Table 7.

The copper atom is surrounded by a distorted octahedron. This behaviour, which occurs in most Cu(II) compounds is an example of the so-called Jahn-Teller effect.[35] Table 8 shows, for purposes of comparison, the bonding distances in some other Cu^{2+} compounds,[35] where this effect is also obvious.

Table 7. Cu—N bond distances, found in some copper compounds,[45] compared with those found in [Cu(N₃)₂(NH₃)₂].

Substance	Cu—N bond distance (Å)
α-Cu(NH₃)₂Br₂	1.93
Cu(C₄H₇N₂O₂)₂	1.94
Cu(C₅H₈NO₂)₂(H₂O)₂	1.99
C₂H₆N₂Cu₂Cl₂	1.99
Cu(NH₃)₂Cl₂	2.03
[Cu(CN)₂]ₙ	2.05
Cu(NH₃)₄SO₄·H₂O	2.05
[Cu(N₃)₂(NH₃)₂]	{ 1.99 2.05

Table 8. Atomic distances found in some Cu²⁺-compounds,[35] compared with those found in [Cu(N₃)₂(NH₃)₂].

Compound	Atomic distances		
CuCl₂	4 Cl at 2.3 Å	2 Cl at 3.0 Å	
CuBr₂	4 Br at 2.4 Å	2 Br at 3.2 Å	
CuF₂	4 F at 1.9 Å	2 F at 2.3 Å	
Cu₂(OH)₂(CO₃)	4 O (OH) at 2.0 Å	2 O at 2.7 Å	
CuCl₂·2H₂O	2 H₂O at 2.0 Å	2 Cl at 2.3 Å	2 Cl at 3.0 Å
CuCl₂·2py	2 N at 2.0 Å	2 Cl at 2.3 Å	2 Cl at 3.1 Å
Cu(N₃)₂(NH₃)₂	4 N at 2.0 Å	2 N at 2.6 Å, 2.7 Å	

The chains of octahedra from which the structure can be supposed to be built up are joined by hydrogen bonds of the type N—H···N as indicated by the IR-spectrum. It is most probable that the hydrogen bonds are developed to the three atoms which lie nearest (3.18 Å, 3.24 Å, 3.26 Å), the geometrical configuration being also favourable in this case (Fig. 3b). In the case of the weak hydrogen bonds, however, it is not necessary that the ammine group develops three strictly directed bonds, and it may also be possible that the nitrogen atom at a distance of 3.31 Å is partially hydrogen bonded.

Two somewhat different azide groups appear to exist in this compound. The measured nitrogen-nitrogen distances (1.174 Å, 1.142 Å, and 1.186 Å, 1.139 Å, respectively) can be compared with the corresponding distances in the aforementioned compound [CoN₃(NH₃)₅] (N₃)₂,[9] in which the nitrogen-nitrogen distances in the asymmetric azide group bonded to Co, have been calculated to be 1.208 Å and 1.145 Å. The values for the angles Cu(1)—N(2)—N(3) and Cu(1)—N(5)—N(6) (116.3° and 121.4°, respectively) lie within the region reported for asymmetric azides, *e.g.* 124.8° in [CoN₃(NH₃)₅] (N₃)₂[9] and 112.7° in HN₃.[36] The azide groups are almost linear, the angles in the two groups being 177.5° and 177.6°, respectively. This can be compared with the structure of [CoN₃(NH₃)₅] N₃)₂, in which the three

nitrogen atoms in the azide groups are reported to make angles of 177.5° and 179.5° [9].

The coordination relations are not the same for the two azide groups. One group, $N(2)-N(3)-N(4)$, is bonded to three different copper atoms, namely through $N(2)$ to one copper atom at a short distance of 2.05 Å and also through $N(2)$ to another copper atom at a longer distance of 2.56 Å, and through $N(4)$ to a third copper atom at a distance of 2.67 Å (Fig. 3a). It is reasonable to expect that such a relationship would tend to make the bond distances within the azide group less different. The other azide group $N(5)-N(6)-N(7)$ is, however, only bonded to one copper atom, namely through $N(5)$ at the short distance of 2.05 Å, so it is less affected by the environment of the other atoms and should thus be more markedly asymmetric.

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