The Crystal Structure of $[Cu(N_3)_2(C_5H_5N)_2]$

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The crystal structure of $[Cu(N_3)_2(C_5H_5N)_2]$ has been determined
by single crystal X-ray diffraction methods.

The crystals belong to the space group $Cmc2_1$ (No. 36).
The unit cell contains four formula units and has the dimensions
$a = 13.884 \pm 0.002$ Å, $b = 13.646 \pm 0.002$ Å, $c = 6.403 \pm 0.002$ Å, and
$V = 1213.1$ Å³. The coordination around the copper atom is distorted
octahedral, with four shorter (1.98 ± 0.03 Å, 2.01 ± 0.02 Å, 2.04 ± 0.01
Å and 2.04 ± 0.01 Å) and two longer (2.50 ± 0.03 Å and 2.76 ± 0.03 Å)
copper-ligand bonds. The octahedra are linked together to form chains
by the sharing of corners. The azido groups are linear and seem to be
asymmetric, the nitrogen-nitrogen distances and their standard devia-
tions having been determined to be 1.14 ± 0.04 Å, 1.08 ± 0.04 Å and
1.23 ± 0.03 Å, 1.19 ± 0.04 Å, respectively.

The R-value of the proposed structure is 0.078.

The infrared spectrum of $[Cu(N_3)_2(C_5H_5N)_2]$ has also been reg-
istered.

$\mathbf{M}$any investigations have been performed in order to attempt to elucidate
the properties of the explosive inorganic metal azides,[1-3] which are of
great technical importance. In order to obtain information concerning the
structural features of such compounds the author is performing an investiga-
tion of the crystal structures of a group of related inorganic metal azides.
As part of this investigation the crystal structures of $[Cu(N_3)_2(NH_3)_2]$[4] and
$Cu(N_3)_2$[5,6] have already been determined, while the structure of
$[Cu(N_3)_2(C_5H_5N)_2]$ is presented in this paper.

The compound $[Cu(N_3)_2(C_5H_5N)_2]$ was first prepared by Dennis and Isham,[7]
but other methods of preparation have since been published.[8,9] The products
formed have been described as brown, brownish-green or green. According
to Cirulis and Straumanis[9] there are two modifications of $[Cu(N_3)_2(C_5H_5N)_2]$,
one green and one brown; both, however, are reported to give the same powder
photographs.

EXPERIMENTAL

Preparation. $[Cu(N_3)_2(C_5H_5N)_2]$ was prepared in two different ways: (a) Copper azide was precipitated from a solution of 1.25 g $CuSO_4 \cdot 5H_2O$ in 25 ml water by the addition of a solution of 0.65 g NaN_3 in 6.5 ml water. The precipitate formed was filtered off and dissolved in warm pyridine. From this solution $[Cu(N_3)_2(C_5H_5N)_2]$ crystallized as green crystals.[8] (b) 10.0 g pyridine was poured into a solution of 6.5 g $Cu(NO_3)_2 \cdot 3H_2O$ in 10 ml water and a solution of 5.0 g NaN_3 in 15 ml hot water was added. When the solution cooled green crystals appeared which were then recrystallized from pyridine.[9]

The crystals of $[Cu(N_3)_2(C_5H_5N)_2]$ which were used for the X-ray investigation were needle-shaped, the dimensions being of the magnitude of $0.02 \times 0.02 \times 0.08$ mm. The crystals disintegrated in the X-ray radiation.

Analysis. The amount of copper in $[Cu(N_3)_2(C_5H_5N)_2]$ was determined by means of electrolysis [10] and the azide content was determined by titration with a Ce(IV) solution.[11] (Found: Cu 21.3; N_3^- 27.3. Calc. for $[Cu(N_3)_2(C_5H_5N)_2]$: Cu 20.8; N_3^- 27.5).

STRUCTURE INVESTIGATION

X-Ray methods. Green, thin, needle-shaped single crystals of $[Cu(N_3)_2(C_5H_5N)_2]$ were used to collect the intensity data. They were rotated about the three crystallographical axes, but because the crystals were unstable, a new crystal had to be mounted in a capillary for each layer line. Weissenberg photographs were registered for the eighteen zones ($hk0-hk4$, $h0l-h3l$, $h7l$, $0kl-7kl$) using multiple film equi-inclination techniques and CuKα-radiation.

In order to determine accurate cell dimensions, X-ray powder photographs of $[Cu(N_3)_2(C_5H_5N)_2]$ were taken in a Guinier focusing camera, using CuKα_1-radiation ($\lambda = 1.54050$ Å) and $Pb(NO_3)_2$ ($a = 7.8564$ Å [12]) as an internal standard.

Unit cell and space group. The crystals were found to be orthorhombic, and the dimensions of the cell were determined from the Guinier photographs using the Algol Programme Xalg Powder.[13] The values obtained were $a = 13.884 \pm 0.002$ Å, $b = 13.646 \pm 0.002$ Å, $c = 6.403 \pm 0.002$ Å, and $V = 1213.1$ Å^3. Observed and calculated $\sin^2\theta$-values are given in Table 1, together with observed and calculated intensities.

A measure of the density of the crystals was obtained by the flotation method using mixtures of $CHBr_3$ and CCl_4. The density found was 1.72 g/cm^3, which yields four formula units per unit cell ($\varrho_{calc.} = 1.67$ g/cm^3).

From the X-ray photographs it was obvious that the following conditions of reflexion were obeyed: hkl: $h+k = 2n$; $h0l$: $l = 2n$. This is characteristic for the space groups $Cmc2_1$ (No. 36), $Ama2$ (No. 40) and $Cmcm$ (No. 63).[12]

Determination of the structure. The intensities of the reflexions were estimated by visual comparison with a standard scale. The values obtained were corrected for Lorentz and polarisation effects by the programme "General data reduction".[14] No correction was applied for absorption, since the size of the crystals was always chosen so that μR was ≤ 0.2.

Calculations were commenced, assuming the space group to be $Cmcm$ (No. 36). A two-dimensional Patterson summation, based on the $hk0$-reflexions was undertaken, using a Fourier programme.[15] The largest peaks, discounting that at the origin, were observed at (0.00, 0.23), (0.50, 0.50), and (0.50, 0.27). These peaks could be explained if the copper atom was situated in the four-

Table 1. X-Ray powder diffraction data for [Cu(N$_3$)$_2$(C$_5$H$_5$N)$_2$]. Guinier camera. CuKα_1 radiation ($\lambda = 1.54050$ Å). The refinement of the cell dimensions is based on the unambiguously indexed reflexions.

h k l	$10^6 \sin^2 \theta_{obs}$	$10^6 \sin^2 \theta_{calc}$	I_{obs}	I_{calc} (rel. scale)
1 1 0	6 255	6 263	vst	210
2 0 0	12 271	12 310	st	25
1 1 1	20 672	20 736	vst	68
0 2 1	27 199	27 216	vst	80
3 1 0	30 887	30 884	st	18
2 2 1	39 496	39 526	m	10
3 1 1	45 284	45 356	m	15
1 3 1	46 181	46 223	m	10
4 0 0	49 205	49 241	st	26
0 4 0	50 905	50 975	vst	77
1 1 2	64 171	64 152	m	11
0 4 1	65 434	65 447	w	5
2 0 2	70 152	70 199	st	24
2 4 1	77 690	77 757	m	10
5 1 0	80 119	80 125	w	5
1 5 0	82 768	82 726	w	6
3 1 2	88 744	88 773	w	4
5 1 1	94 593	94 597	w	4
1 5 1	97 160	97 198	w	2
4 0 2	107 112	107 130	w	2
0 4 2	108 883	108 864	m	7
6 0 0	110 827	110 792	m	13
2 4 2	121 203	121 174	m	8
0 6 1	129 164	129 166	w	5
6 2 1	138 060	138 008	w	4
5 1 2		138 014		2
1 5 2	140 646	140 615	w	5
2 2 3	155 257	155 304	w	4
6 4 0	161 929	161 767	w	2
1 3 3		162 001		4
6 0 2	168 588	168 681	w	4
1 7 1	173 568	173 661	w	3

vst = very strong, st = strong, m = medium, w = weak

fold position 4c with $x=0$ and $y \approx 0.115$. Using the signs of the structure factors thus obtained, an electron density projection on (001) was calculated [15] (Fig. 1). From this projection it was possible to locate the atoms of the pyridine ring and to find their approximate x- and y-coordinates. These atoms were assumed to occupy the eightfold positions 8g of space group *Cmcm*. The azido groups appeared to lie parallel to the b-axis in the projection, but there was too much overlap to make it possible to identify the individual nitrogen atoms. In the extension of the structure determination to three dimensions it became obvious that the structure was not centrosymmetric, and the space group *Cmc2*$_1$ (No. 36) [12] was therefore employed, the copper atom occupying the four-fold position 4a and the atoms of the pyridine ring the eight-fold position 8b. The x- and y-parameters assigned to the atoms were those obtained from the calculations based on the $hk0$-data. The z-parameter of the copper
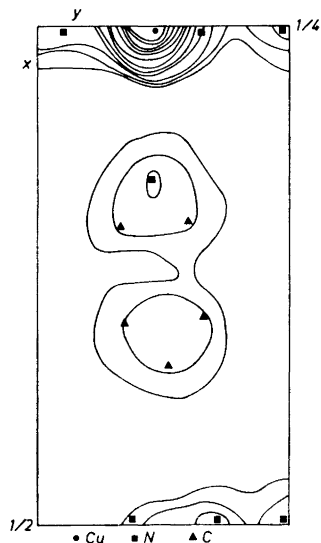
Fig. 1. Electron density projection of $[Cu(N_3)_2(C_5H_5N)_2]$ on (001). Arbitrary units. The final positions of the atoms are indicated.

atom was chosen arbitrarily to be 0.1775, while the z-parameters of the pyridine ring atoms were obtained from geometrical considerations, using the known dimensions of the pyridine ring. A three-dimensional Fourier synthesis, based on these assumptions, using the reflexions from $hk0-hk2$, gave an electron density function which revealed the positions of the individual atoms of the azido groups and yielded preliminary x-, y-, and z-coordinates for all thirteen atoms.

Refinement of the structure. In order to refine the structural parameters, several different least squares calculations were performed using the programme LALS.[16] In the first stages of the refinement, the parameters based on observed reflexions from the three different crystallographic axes were refined separately with isotropic temperature factors for all atoms. The weights of the reflexions were calculated according to Hughes ($w^{-\frac{1}{2}}=F_o$ if $F_o>4\cdot F_{o\ min}$ and $w^{-\frac{1}{2}}=4\cdot F_{o\ min}$ if $F_o<4\cdot F_{o\ min}$). The refinements yielded, for the a-axis data an R-value of 0.075, which was based on 203 independent reflexions, for the b-axis data an R-value of 0.105, based on 87 independent reflexions and for the c-axis data an R-value of 0.081, based on 177 independent reflexions.

The sets of data were then combined. Two slightly different methods of refinement were used and the results were compared. In the first method all observed reflexions from the three axes were treated as independent reflexions, thus giving a total of 467 independent reflexions, and allowance was made for anisotropic vibration of all atoms. In the second method the average values of the observed structure factors were used for the reflexions registered more than once, thus giving a total of 272 independent reflexions. In this case all atoms were refined isotropically. In both cases Hughes's weighting scheme was used. There was no statistical difference between the results of the two methods, and R-values and standard deviations were of the same

magnitude. It was, however, apparent from both weight analyses, that the greatest deviations occurred for the strongest reflexions. Cruickshank's weighting scheme $(w^{-1}=a+F_o+cF_o{}^2+dF_o{}^3)$ was therefore employed in order to be able to give the stronger reflexions less weight. The constants were varied in order to see the effect on the weighting scheme, the R-value and the standard deviations. The final cycles of refinement were performed with the reflexion material of 272 independent reflexions, and the weight constants used were $a=11.36$, $c=0.00736$, and $d=0$, a total of 45 parameters being refined. When the parameter shifts were less than 1 % of the standard deviations the refinement was terminated. The reliability index was then 0.078, and a difference electron density map at this stage showed no spurious peaks. The standard deviations calculated were relatively high, but this may be attributed to the experimental difficulties due to the instability of the compound, making it necessary to collect the intensity data from a large number of different crystals. The resulting atomic parameters are given in Table 2 and observed and calculated structure factors are listed in Table 3.

Table 2. Atomic coordinates (expressed as fractions of the cell edges) and isotropic temperature factors of the form $\exp[-B(\sin^2\theta/\lambda^2]$. The standard deviations are given in parentheses. Space group $Cmc2_1$.

Atom		x	y	z	B
Cu	$4a$	0.5000	0.3873(3)	0.1775	6.16(11)
N(1)	$4a$	0.5000	0.2543(18)	0.3003(44)	5.22(50)
N(2)	$4a$	0.5000	0.1823(17)	0.2114(40)	4.53(48)
N(3)	$4a$	0.5000	0.1120(23)	0.1353(70)	8.65(88)
N(4)	$4a$	0.5000	0.5250(13)	0.0662(42)	4.49(50)
N(5)	$4a$	0.5000	0.5939(12)	0.1892(53)	3.76(40)
N(6)	$4a$	0.5000	0.6630(20)	0.3028(46)	5.79(52)
N(7)	$8b$	0.3530(9)	0.3846(9)	0.1754(50)	4.28(24)
C(1)	$8b$	0.3090(16)	0.3468(19)	0.3441(41)	6.02(51)
C(2)	$8b$	0.2077(20)	0.3335(19)	0.3630(38)	7.09(61)
C(3)	$8b$	0.1591(14)	0.3708(14)	0.2128(42)	6.01(55)
C(4)	$8b$	0.2027(20)	0.4077(16)	0.0260(41)	6.97(60)
C(5)	$8b$	0.3008(17)	0.4166(16)	0.0179(36)	5.61(51)

IR-SPECTRUM OF $[Cu(N_3)_2(C_5H_5N)_2]$

The IR-spectrum of $[Cu(N_3)_2(C_5H_5N)_2]$, registered on a Perkin Elmer-421 spectrophotometer, using the KBr technique, is shown in Fig. 2. Most of the bands originate from pyridine, but the strong band at 2030 cm⁻¹ may be accounted for by an antisymmetric stretching frequency of the azido group.[17,18] The weak absorption due to the azido group, which is to be found between 1340 cm⁻¹ and 1180 cm⁻¹,[17] is difficult to locate, since pyridine also shows absorption in this region.

Table 3. Observed and calculated structure factors for $[Cu(N_3)_2(C_5H_5N)_2]$. The columns are h, k, l, $|F_o|$ and $|F_c|$, respectively.

h	k	l	|Fo|	|Fc|
0	4	0	260.0	240.4
0	6	0	39.6	38.4
0	8	0	60.7	60.9
0	10	0	32.3	27.8
0	10	1	30.9	34.9
0	8	1	48.6	50.7
0	6	1	122.0	105.9
0	4	1	88.5	66.9
0	2	1	202.1	171.0
0	10	2	38.1	38.3
0	8	2	58.3	54.6
0	6	2	59.2	60.4
0	4	2	112.3	108.7
0	2	2	87.8	89.5
0	0	2	141.9	152.2
0	10	3	44.9	40.2
0	6	3	43.8	46.2
0	4	3	19.4	20.4
0	2	3	23.6	22.7
0	14	4	6.4	6.7
0	12	4	13.1	13.3
0	10	4	23.6	20.3
0	8	4	25.9	23.4
0	6	4	22.4	23.4
0	4	4	58.0	56.3
0	2	4	6.3	10.1
0	0	4	38.3	38.8
0	2	5	42.0	43.7
0	4	6	28.2	28.7
0	0	6	39.5	38.7
1	1	6	17.3	15.5
1	1	5	20.8	19.4
1	1	4	24.5	26.9
1	1	3	43.4	49.2
1	1	2	65.5	70.8
1	1	1	95.2	96.1
1	1	0	141.5	129.1
1	3	5	27.9	25.1
1	3	4	16.4	16.9
1	3	3	60.0	55.8
1	3	2	36.0	35.8
1	3	1	54.4	58.7
1	3	0	26.7	29.6
1	5	6	20.9	17.7
1	5	4	50.3	48.6
1	5	3	37.7	36.4
1	5	2	73.4	75.8
1	5	1	34.6	40.0
1	5	0	74.7	80.7
1	7	5	10.5	11.6
1	7	3	24.1	22.0
1	7	1	65.9	66.0
1	7	0	14.9	15.8
1	9	4	29.0	24.9
1	9	2	42.6	39.8
1	9	0	45.8	43.1
1	11	3	24.5	21.4
1	11	1	25.6	23.1
1	13	4	9.7	8.1
1	13	2	17.3	12.4
1	15	1	18.3	13.7
2	14	0	19.9	16.8
2	12	0	9.8	10.8
2	10	0	22.4	22.2
2	8	0	49.2	41.0
2	6	0	24.6	24.9
2	4	0	10.0	12.9
2	0	0	99.9	91.8
2	14	1	10.5	9.5
2	10	1	27.4	25.9
2	8	1	38.3	37.8
2	6	1	34.5	35.2
2	4	1	92.9	76.1
2	2	1	60.6	54.1
2	14	2	9.2	9.9
2	10	2	22.2	23.0
2	8	2	17.2	17.7
2	6	2	42.7	44.5
2	4	2	84.3	84.2
2	2	2	15.9	15.9
2	0	2	165.7	156.4
2	6	3	30.6	29.5
2	4	3	17.7	20.4
2	2	3	75.9	74.2
2	10	4	18.1	17.9
2	8	4	8.1	7.9
2	6	4	25.5	27.1
2	4	4	49.2	48.8
2	2	4	16.5	21.0
2	0	4	41.0	44.3
2	10	5	9.2	9.1
2	6	5	9.0	9.2
2	4	5	8.5	12.5
2	2	5	13.9	11.4
2	8	6	7.6	5.7
2	4	6	11.0	8.6
2	0	6	8.6	6.3
2	0	8	8.3	8.2
3	9	0	33.2	31.3
3	7	0	16.4	17.3
3	5	0	42.9	46.5
3	3	0	23.2	26.3
3	1	0	93.0	87.5
3	15	1	12.5	10.3
3	11	1	20.1	15.6
3	7	1	47.4	44.9
3	5	1	39.8	40.9
3	3	1	27.7	29.8
3	1	1	71.4	72.4
3	9	2	27.5	25.3
3	7	2	9.8	9.7
3	5	2	53.6	58.3
3	3	2	26.8	28.8
3	1	2	52.1	51.2
3	7	3	7.4	7.0
3	5	3	33.3	31.5
3	3	3	41.0	41.7
3	1	3	38.0	41.3
3	9	4	16.4	13.5
3	5	4	35.2	35.2
3	3	4	11.7	15.2
3	1	4	15.3	18.6
3	3	5	14.8	11.8
4	14	0	15.9	12.4
4	10	0	15.8	17.2
4	8	0	11.6	13.8
4	6	0	20.4	20.8
4	4	0	47.5	51.2
4	0	0	211.8	192.0
4	8	1	19.8	21.5
4	6	1	18.1	23.2
4	4	1	14.0	18.6
4	2	1	16.3	14.0
4	10	2	19.6	20.0
4	6	2	23.0	22.2
4	4	2	30.8	35.7
4	2	2	47.8	44.8
4	0	2	59.7	61.0
4	10	3	13.0	12.7
4	6	3	11.2	11.7
4	4	3	14.4	15.1
4	2	3	9.4	12.2
4	10	4	13.7	12.4
4	6	4	12.1	11.4
4	4	4	26.2	25.8
4	0	4	9.3	11.0
4	2	5	15.4	11.6
4	4	6	12.5	10.2
4	0	6	14.0	12.6
5	1	4	13.9	14.0
5	1	3	26.3	30.3
5	1	2	44.4	42.4
5	1	1	54.5	55.7
5	1	0	72.2	77.8
5	3	5	16.1	16.5
5	3	4	8.7	8.2
5	3	3	30.7	29.9
5	3	2	25.0	26.8
5	3	1	27.6	31.6
5	3	0	11.6	12.3
5	5	6	14.9	12.6
5	5	4	32.7	32.9
5	5	3	21.1	23.9
5	5	2	46.5	45.8
5	5	1	21.0	23.4
5	5	0	53.9	53.2
5	7	3	11.9	10.4
5	7	2	16.4	6.4
5	7	1	41.1	40.0
5	7	0	9.3	10.0
5	9	4	18.5	17.4
5	9	2	26.5	24.9
5	9	0	28.0	26.0
5	11	1	16.9	12.1
5	13	4	6.8	5.4
6	14	0	15.2	12.5
6	10	0	14.8	17.0
6	8	0	37.8	42.1
6	6	0	19.0	21.5
6	4	0	105.3	100.4
6	0	0	263.7	215.7
6	10	1	25.3	26.2
6	8	1	18.9	21.8
6	6	1	63.6	59.6
6	4	1	16.7	18.9
6	2	1	62.8	66.2
6	14	2	11.1	9.7
6	10	2	20.5	21.9
6	8	2	31.5	30.7
6	6	2	20.6	22.6
6	4	2	75.1	71.8
6	2	2	28.6	33.4
6	0	2	102.0	106.3
6	10	3	23.1	21.4
6	6	3	31.8	31.1
6	4	3	12.6	13.1
6	2	3	37.0	36.6
6	12	4	6.0	7.2
6	10	4	13.3	14.3
6	8	4	13.1	13.7
6	6	4	11.5	13.6
6	4	4	41.2	40.2
6	0	4	31.1	32.5
6	4	5	13.8	14.8
6	2	5	22.5	23.1
6	4	6	16.7	16.4
6	0	6	19.0	19.8
7	1	5	12.7	13.9
7	1	4	20.4	20.2
7	1	3	28.5	28.0
7	1	2	40.7	43.5
7	1	1	46.2	51.9
7	1	0	73.0	70.1
7	3	5	11.7	15.3
7	3	4	12.0	13.6
7	3	3	37.3	36.6
7	3	2	16.9	16.2
7	3	1	33.4	34.9
7	3	0	26.4	27.6
7	5	4	33.8	31.4
7	5	3	18.9	20.8
7	5	2	57.9	50.1
7	5	1	22.4	24.1
7	5	0	46.4	45.9
7	7	3	15.0	15.9
7	7	1	41.7	39.6
7	7	0	9.7	10.1
7	9	4	17.0	15.8
7	9	2	28.8	28.0
7	9	0	27.5	29.5
7	11	1	16.3	17.1
8	8	0	25.8	26.1
8	4	0	24.0	26.1
8	0	0	63.8	68.2
8	6	1	25.5	28.5
8	4	1	25.6	26.5
8	4	2	51.4	49.2
8	0	2	79.5	78.8
8	2	3	44.8	43.6
8	10	4	9.6	11.3
8	8	4	6.9	6.5
8	6	4	11.9	14.9
8	4	4	33.1	31.4
8	2	4	7.0	10.3
8	0	4	30.1	29.7
9	7	0	6.2	6.5
9	5	0	26.5	29.5
9	1	0	34.2	36.7
9	7	1	22.5	22.2
9	1	1	24.7	27.8
9	1	2	32.3	28.6
9	1	3	22.4	22.7
9	9	4	9.3	8.6
9	5	4	16.9	19.0
9	3	4	7.3	8.6
9	1	4	8.6	10.6
10	4	0	25.0	25.0
10	0	0	73.8	74.2
10	10	4	5.4	6.2
10	4	4	7.4	6.9
11	1	0	24.8	25.9
11	7	1	9.3	9.1
11	9	4	6.3	5.4
11	5	4	10.8	11.0
12	0	0	26.3	31.5
12	0	2	34.9	34.3
12	6	4	5.9	7.0
12	4	4	14.5	12.9
13	7	1	9.3	10.5
13	5	4	8.8	10.8
14	0	0	25.7	31.7
14	0	4	9.5	7.5

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of one formula unit of the compound $[Cu(N_3)_2(C_5H_5N)_2]$ projected along the c-axis is reproduced in Fig. 3. Fig. 4 illustrates how the structure is built up by the linking of somewhat distorted octahedra and Fig. 5 shows the packing of the pyridine rings. Atomic distances and angles have been calculated by the programme DISTAN [16] and are given in Tables 4 and 5. A comparison of corresponding distances found in the related structures $Cu(N_3)_2$,[6,5] $[Cu(N_3)_2(NH_3)_2]$,[4] and $[Cu(N_3)_2(C_5H_5N)_2]$ is given in Table 6.
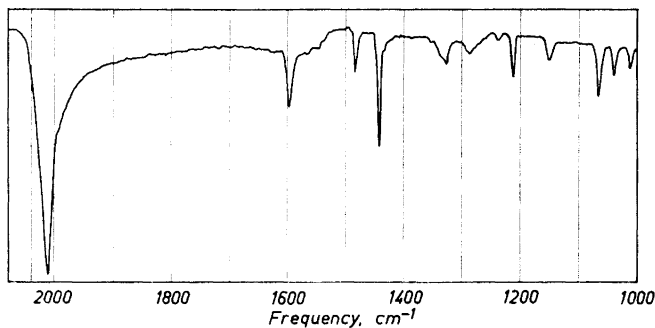
Fig. 2. Infrared spectrum of [Cu(N₃)₂(C₅H₅N)₂]. (The monochromator was changed at 2000 cm⁻¹).
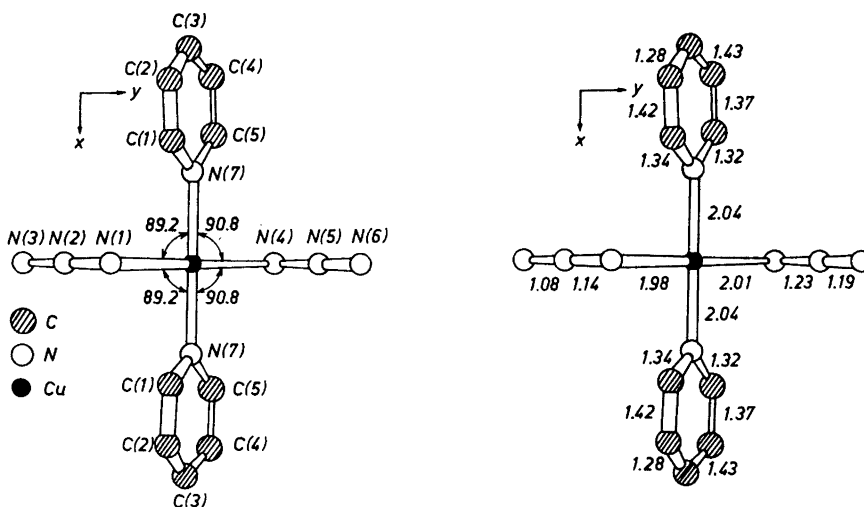
Fig. 3. A formula unit of [Cu(N₃)₂(C₅H₅N)₂] projected along the c-axis.

The copper atom is surrounded by four nitrogen atoms in an almost square-planar configuration (Fig. 3), two of the nitrogen atoms each being end atoms of an azido group, and the other two each originating from a pyridine ring. The distances from the central copper atom to the nitrogen atoms of the two azido groups are 1.98±0.03 Å and 2.01±0.02 Å, and to the nitrogen atoms of the pyridine rings 2.04±0.01 Å, both distances being equal owing to symmetry reasons. The plane containing the central copper atom and these four nitrogen atoms makes an angle of 43° with the plane of the pyridine ring. Besides these four nearest neighbours, the copper atom, has, as expected, two other neighbouring atoms at distances of 2.76±0.03 Å and

Table 4. Interatomic distances in [Cu(N$_3$)$_2$(C$_5$H$_5$N)$_2$]. The standard deviations are given in parentheses. The numbers enclosed in square brackets indicate fractional atomic coordinates.

a) Cu—N distances within the coordination sphere:

						Distance (Å)
Cu[0.50,	0.39,	0.18]—N(1)[0.50,	0.25,	0.30]		1.979(26)
Cu[0.50,	0.39,	0.18]—N(4)[0.50,	0.52,	0.07]		2.010(20)
Cu[0.50,	0.39,	0.18]—N(7)[0.35,	0.38,	0.18]		2.041(12)
Cu[0.50,	0.39,	0.18]—N(4)[0.50,	0.48,	0.57]		2.761(25)
Cu[0.50,	0.39,	0.18]—N(6)[0.50,	0.34,	−0.20]		2.496(29)

b) N—N distances within the azido groups:

N(1)[0.50,	0.25,	0.30]—N(2)[0.50,	0.18,	0.21]		1.135(36)
N(2)[0.50,	0.18,	0.21]—N(3)[0.50,	0.11,	0.14]		1.076(43)
N(1)[0.50,	0.25,	0.30]—N(3)[0.50,	0.11,	0.14]		2.210(43)
N(4)[0.50,	0.52,	0.07]—N(5)[0.50,	0.59,	0.19]		1.226(34)
N(5)[0.50,	0.59,	0.19]—N(6)[0.50,	0.66,	0.30]		1.191(37)
N(4)[0.50,	0.52,	0.07]—N(6)[0.50,	0.66,	0.30]		2.416(36)

c) N—C and C—C distances within the pyridine ring:

N(7)[0.35,	0.38,	0.18]—C(1)[0.31,	0.35,	0.34]		1.344(37)
N(7)[0.35,	0.38,	0.18]—C(5)[0.30,	0.42,	0.02]		1.316(35)
C(1)[0.31,	0.35,	0.34]—C(2)[0.21,	0.33,	0.36]		1.424(36)
C(2)[0.21,	0.33,	0.36]—C(3)[0.16,	0.37,	0.21]		1.280(35)
C(3)[0.16,	0.37,	0.21]—C(4)[0.20,	0.41,	0.02]		1.433(36)
C(4)[0.20,	0.41,	0.03]—C(5)[0.30,	0.42,	0.02]		1.369)37)

d) Selected distances other than bond distances:

C(2)[0.71,	0.17,	−0.14]...N(3)[0.50,	0.11,	0.14]		3.451(36)
C(3)[0.34,	0.13,	−0.29]...N(3)[0.50,	0.11,	0.14]		3.500(36)

Table 5. Angles in [Cu(N$_3$)$_2$(C$_5$H$_5$N)$_2$]. Notation as in Table 4.

a) N—Cu—N and Cu—N—N angles within the coordination sphere:

			Angle (°)
N(1)[0.50, 0.26, 0.30]—Cu [0.50, 0.39, 0.18]—N(7)[0.35, 0.39, 0.18]			89.2(0.5)
N(4)[0.50, 0.52, 0.07]—Cu [0.50, 0.39, 0.18]—N(7)[0.35, 0.39, 0.18]			90.8(0.5)
N(4)[0.50, 0.52, 0.07]—Cu [0.50, 0.39, 0.18]—N(6)[0.50, 0.34,−0.20]			85.2(1.0)
N(1)[0.50, 0.25, 0.30]—Cu [0.50, 0.39, 0.18]—N(6)[0.50, 0.34,−0.20]			97.4(1.0)
N(1)[0.50, 0.26, 0.30]—Cu [0.50, 0.39, 0.18]—N(4)[0.50, 0.48, 0.57]			92.3(0.9)
N(4)[0.50, 0.52, 0.07]—Cu [0.50, 0.39, 0.18]—N(4)[0.50, 0.48, 0.57]			85.1(0.5)
N(4)[0.50, 0.48, 0.57]—Cu [0.50, 0.39, 0.18]—N(7)[0.35, 0.39, 0.18]			90.8(0.8)
N(6)[0.50, 0.34,−0.20]—Cu [0.50, 0.39, 0.18]—N(7)[0.35, 0.39, 0.18]			89.4(0.9)
Cu [0.50, 0.39, 0.18]—N(1)[0.50, 0.25, 0.30]—N(2)[0.50, 0.18, 0.21]			126.5(2.5)
Cu [0.50, 0.39, 0.18]—N(4)[0.50, 0.52, 0.07]—N(5)[0.50, 0.59, 0.19]			119.2(2.2)

b) N—N—N angles within the azido groups:

N(1)[0.50, 0.25, 0.30]—N(2)[0.50, 0.18, 0.21]—N(3)[0.50, 0.11, 0.14]			176.9(4.1)
N(4)[0.50, 0.53, 0.07]—N(5)[0.50, 0.59, 0.19]—N(6)[0.50, 0.66, 0.30]			177.6(3.2)

c) angles within the pyridine ring:

N(7)[0.35, 0.39, 0.18]—C(1) [0.31, 0.35, 0.34]—C(2) [0.21, 0.33, 0.36]			124.5(2.2)
C(1) [0.31, 0.35, 0.34]—C(2) [0.21, 0.33, 0.36]—C(3) [0.16, 0.37, 0.21]			114.0(2.3)
C(2) [0.21, 0.33, 0.36]—C(3) [0.16, 0.37, 0.21]—C(4) [0.20, 0.41, 0.03]			122.9(2.2)
C(3) [0.16, 0.37, 0.21]—C(4) [0.20, 0.41, 0.03]—C(5) [0.30, 0.42, 0.02]			118.9(2.3)
N(7)[0.35, 0.39, 0.18]—C(5) [0.30, 0.42, 0.02]—C(4) [0.20, 0.41, 0.03]			119.3(2.1)
C(1) [0.31, 0.35, 0.34]—N(7)[0.35, 0.39, 0.18]—C(5) [0.30, 0.42, 0.02]			119.5(1.7)

Table 6. Comparison of the distances in $Cu(N_3)_2$,[6] $[Cu(N_3)_2(NH_3)_2]$,[4] and $[Cu(N_3)_2(C_5H_5N)_2]$. The standard deviations are given in parentheses.

	$Cu(N_3)_2$ (Å)	$[Cu(N_3)_2(NH_3)_2]$ (Å)	$[Cu(N_3)_2(C_5H_5N)_2]$ (Å)
Four shorter Cu—N distances	$1.99(1)^a$ $1.99(1)^a$ $2.00(1)^a$ $2.00(1)^a$	$2.05(1)^a$ $2.05(1)^a$ $1.99(1)^b$ $1.99(1)^b$	$1.98(3)^a$ $2.01(2)^a$ $2.04(1)^c$ $2.04(1)^c$
Two longer Cu—N distances	2.56(1) 2.71(1)	2.56(1) 2.67(1)	2.50(3) 2.76(3)
N—N distances in the azido group coordinated at one end only	1.21(1) 1.09(2)	1.19(1) 1.14(1)	1.14(4) 1.08(4)
N—N distances in the azido group coordinated at both ends	1.21(1) 1.13(1)	1.17(1) 1.14(1)	1.23(3) 1.19(4)

^{a} N part of an azido group.
^{b} N part of an ammino group.
^{c} N part of a pyridine ring.
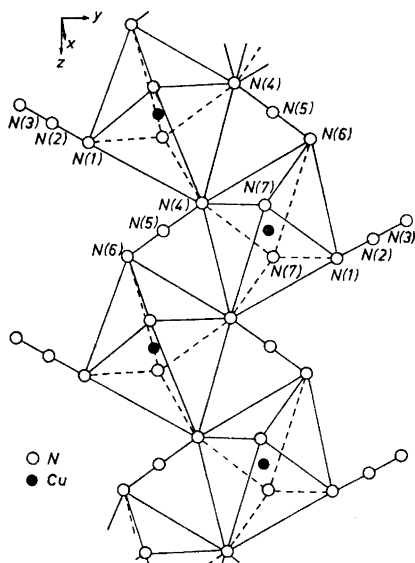
Fig. 4. The chain of octahedra from which the structure is built up. The pyridine rings, which are directed perpendicular to the yz-plane, have not been drawn in full, but their positions are indicated by their nitrogen atoms, N(7).
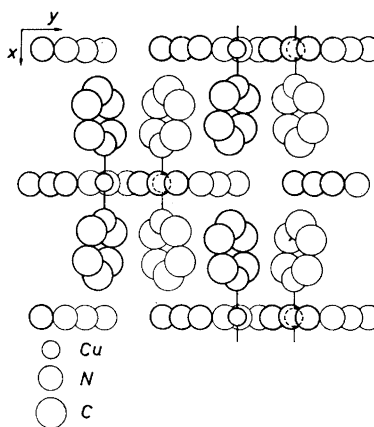
Fig. 5. The packing of the azido groups and the pyridine rings as projected along the c-axis. The copper atoms lie in the planes perpendicular to the a-axis, which are built up from the azido groups.

2.50±0.03 Å, forming an octahedron which is elongated in one direction. All Cu—N distances are in agreement with corresponding distances found in the related structures of $Cu(N_3)_2$ and $[Cu(N_3)_2(NH_3)_2]$ (see Table 6), and in other known structures.[19]

As shown in Fig. 4, the structure can be visualised as being built up of octahedra linked together to form chains running parallel to the c-axis. The octahedra are linked together through a common corner as well as through an azido group. The coupling within the chains is the same as was found in $[Cu(N_3)_2(NH_3)_2]$.[4] The pyridine rings are directed perpendicular to the chains of octahedra. The oblique packing of the rings from different chains is illustrated in Fig. 5, the angle between two neighbouring pyridine rings being 50°. The distances between a pyridine ring of one chain to the nearest azido group of a neighbouring chain are of van der Waals order, the shortest C$\cdots$N distances being 3.45±0.04 Å and 3.50±0.04 Å (Table 4).

There are two crystallographically different azido groups with different structural environments. Thus the azido group N(1)—N(2)—N(3) (Fig. 4) is only coordinated to one copper atom, namely through N(1) at the short distance of 1.98 Å. The other azido group N(4)—N(5)—N(6) is, however, coordinated to three different copper atoms, namely through N(4) to one copper atom at a short distance of 2.01 Å and to another at a long distance of 2.76 Å and through N(6) to a third copper atom at the rather long distance of 2.50 Å. The nitrogen-nitrogen distances within N(1)—N(2)—N(3) are 1.14±0.04 Å and 1.08±0.04 Å, and within the other azido group, N(4)—N(5)—N(6), 1.23±0.03 Å and 1.19±0.04 Å. In both cases the longest N—N distances are those which are closest to the Cu—N bond. The azido group which is only coordinated at one end (N(1)—N(2)—N(3)) is thus shorter (N(1)$\cdots$N(3)=2.21±0.04Å) than the azido group (N(4)—N(5)—N(6)), which is coordinated at both ends to different copper atoms (N(4)$\cdots$N(6)=2.42±0.04 Å). Both azido groups thus seem to be asymmetric, though the differences in the lengths of the N—N bonds are not significant. Asymmetric azido groups were also found in the compounds $Cu(N_3)_2$ and $[Cu(N_3)_2(NH_3)_2]$ (Table 6). In both these compounds there were also two crystallographically different azido groups the degree of asymmetry of which seemed to be different. This was, moreover, supported by the IR-spectra, where the strong absorption band just above 2000 cm^{-1} showed a slight splitting. In $[Cu(N_3)_2(C_5H_5N)_2]$ it is difficult to draw conclusions as to differences in the degree of asymmetry of the two azido groups, although there is a slight indication that the situation is similar to that in $[Cu(N_3)_2(NH_3)_2]$ and $Cu(N_3)_2$, namely that the azido group coordinated at one end only is more asymmetric than that coordinated at both ends. It is, however, surprising that the strong antisymmetric stretching band observed at 2030 cm^{-1} in the IR-spectrum (Fig. 2), although a little broadened, is not split. The angle between the azido group N(1)—N(2)—N(3) and the Cu—N bond is 126.5±2.5°, and that between the azido group N(4)—N(5)—N(6) and the Cu—N bond is 119.2±2.2°. These values may be compared with those found in other compounds with asymmetric azido groups where the values reported lie in a rather broad interval around 120°.[20,21] The azido groups are linear within the limits of experimental error, the angles in the two groups being 176.9±4.1° and 177.6±3.2°, respectively.

The pyridine ring is planar, and the best plane to fit the atoms of the ring was obtained by least squares calculation using the programme PLANE-FIT.[16] The equation of the plane (Cartesian coordinates) is $0.0426X - 0.9061Y - 0.4209Z + 5.0185 = 0$ (X, Y, and Z in Å), and the distances (d) of the atoms to this plane are $d_{N(7)} = -0.002$ Å, $d_{C(1)} = -0.015$ Å, $d_{C(2)} = 0.039$ Å, $d_{C(3)} = -0.046$ Å, $d_{C(4)} = 0.027$ Å and $d_{C(5)} = -0.004$ Å, which means that all six atoms lie in the plane within the limits of experimental error. The C—N distances of the pyridine ring were found to be 1.34 ± 0.04 Å and 1.32 ± 0.04 Å and the C—C distances to be 1.42 ± 0.04 Å, 1.28 ± 0.04 Å, 1.43 ± 0.04 Å and 1.37 ± 0.04 Å (Table 4). The C—N—C angle in the ring is $119.5 \pm 1.7°$, the N—C—C angles are $119.3 \pm 2.1°$ and $124.5 \pm 2.2°$ and the C—C—C angles $114.0 \pm 2.3°$, $122.9 \pm 2.2°$ and $118.9 \pm 2.3°$ (Table 5). These values may be compared with those found for pure pyridine,[22,23] where the C—N distances reported are 1.329 Å, the C—C distances 1.401 Å and 1.402 Å, the C—N—C angle 117.6°, the N—C—C angles 124.0°, and the C—C—C angles 118.1° and 118.4°. There thus seems to be no appreciable distortion of the pyridine ring in [Cu(N$_3$)$_2$(C$_5$H$_5$N)$_2$] apart from a slight shortening of the distance between C(2) and C(3) for which, however, there seems to be no chemical reason.

The Lorentz and polarisation correction, and the Patterson and electron density syntheses were performed on a SAAB D21 computer. The least squares refinements, the calculations of bond distances and angles and the calculation of the plane of the pyridine ring were performed on an IBM 360/50 computer. All computer calculations were performed at the Gothenburg Universities Computing Centre.

REFERENCES

1. Evans, B. L., Yoffe, A. D. and Gray, P. *Chem. Rev.* **59** (1959) 515.
2. Gray, P. *Quart. Rev. (London)* **17** 4 (1963) 441.
3. Lamnevik, S. and Söderquist, R. *Private communication.*
4. Agrell, I. *Acta Chem. Scand.* **20** (1966) 1281.
5. Agrell, I. *Acta Chem. Scand.* **21** (1967) 2647.
6. Agrell, I. and Lamnevik, S. *Acta Chem. Scand.* **22** (1968) 2038.
7. Dennis, L. M. and Isham, H. J. *J. Am. Chem. Soc.* **29** (1907) 19.
8. Strecker, W. and Schwinn, E. *J. prakt. Chem.* **152** (1939) 210.
9. Cirulis, A. and Straumanis, M. *Z. anorg. Chem.* **251** (1943) 349.
10. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quant. Inorg. Analysis,* 3rd Ed., Macmillan, London 1952, p. 408.
11. Arnold, J. W. *Ind. Eng. Chem. Anal. Ed.* **17** (1945) 215.
12. *International Tables for X-ray Crystallography,* Kynoch Press, Birmingham 1959.
13. Lindqvist, O. and Wengelin, F. *Private communication.*
14. Abrahamsson, S. and Larsson, K. *Arkiv Kemi* **24** (1965) 383.
15. Larsson, K. *Arkiv Kemi* **23** (1964) 17.

16. Modified programmes in use at this Department, LALS was originally written by
    Gantzel, R., Sparks, K. and Trueblood, K., DISTAN by Zalkin, A. and PLANEFIT
    by Blow, D. M.
17. Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, Methuen 1958, p. 273.
18. Nakamoto, K. *Infrared Spectra of Inorg. and Coordination Compounds*, Wiley, New
    York 1963, p. 176.
19. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical
    Society, London 1958, Suppl. 1956—1959.
20. Palenik, G. J. *Acta Cryst.* **17** (1964) 360.
21. Amble, E. and Daily, B. P. *J. Chem. Phys.* **18** (1950) 1422.
22. Bak, B., Hansen, L. and Rastrup-Andersen, I. *J. Chem. Phys.* **22** (1954) 2013.
23. Liquori, A. M. and Vaciago, A. *Ric. Sci. Suppl.* **26** (1956) 1848.