

## The Crystal Structure of $\text{Cu}(\text{N}_3)_2$

INGELA AGRELL

*Department of Inorganic Chemistry, Chalmers Institute of Technology, and University of Göteborg, Göteborg, Sweden*

The crystal structure of  $\text{Cu}(\text{N}_3)_2$  has been determined by single crystal X-ray methods.

The crystals belong to the space group *Pnma* (No. 62) and the unit cell contains four formula units. The unit cell dimensions are  $a = 13.481 \pm 0.002 \text{ \AA}$ ,  $b = 3.084 \pm 0.001 \text{ \AA}$ ,  $c = 9.076 \pm 0.002 \text{ \AA}$ , and  $V = 377.32 \text{ \AA}^3$ . The coordination around the copper atom is distorted octahedral, with four shorter (1.98  $\text{\AA}$ ) and two longer (2.60  $\text{\AA}$  and 2.70  $\text{\AA}$ ) copper-ligand bonds. The octahedra are linked together by the sharing of edges to form double chains, which are then coupled by azide groups to form a three-dimensional net. The azide groups are asymmetric, and the nitrogen-nitrogen distances and their standard deviations have been determined to be  $1.232 \pm 0.018 \text{ \AA}$ ,  $1.097 \pm 0.020 \text{ \AA}$ , and  $1.189 \pm 0.020 \text{ \AA}$ ,  $1.100 \pm 0.028 \text{ \AA}$ , respectively.

The reliability index of the proposed structure is 0.063.

The explosive inorganic azides, *e.g.* copper(II)azide, lead(II)azide, and silver azide are of great technical importance. The formation of copper(II)-azide in ammunition containing lead azide has, for instance, provided many problems,<sup>6</sup> and it is therefore of great interest to study the crystal structures of these compounds in order to characterize them and to attempt to explain their tendency to explode violently.

There appears to be a relationship between the explosivity and the structure of the azide group, but no conclusions can be drawn until accurate crystal structure determinations have been performed. Up to now, there are, besides this investigation, only two crystal structure determinations of inorganic azides in which asymmetry in the azide group has been ascertained, namely  $[\text{CoN}_3(\text{NH}_3)_5](\text{N}_3)_2$ ,<sup>9</sup> and  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$ .<sup>10</sup> As a part of a series of investigations of the crystal structures of such inorganic azides, the author has now determined the crystal structures of  $\text{Cu}(\text{N}_3)_2$  and  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ , the former of which is presented in this paper. The structure of  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  is under refinement.

Copper(II)azide was first prepared by Curtius and Rissom,<sup>1</sup> who also examined its explosive properties. Straumanis and Cirulis<sup>2</sup> synthesised

copper(II)azide by various different methods. They determined the cell constants to be 13.225 Å, 3.068 Å, and 9.226 Å and the density to be about 2.2 g/cm<sup>3</sup>. Since then copper(II)azide has been investigated especially with a view to elucidating its explosive properties.<sup>3-8</sup>

### EXPERIMENTAL

*Preparation.* Copper(II)azide was prepared according to a method given by Straumanis and Cirulis:<sup>2</sup> Excess 1 % HN<sub>3</sub> is poured on to powdered copper and the mixture is allowed to stand in a stoppered flask for about three months. Black-brown crystals of copper(II)azide eventually appear.

Because of the explosivity of Cu(N<sub>3</sub>)<sub>2</sub>, all preparations were carried out on a very small scale.

The crystals were needle-shaped and mostly very thin, those being used for the X-ray work being about 0.01 mm thick and 0.06 mm long.

*Analysis.* Since only a very small amount of the sample was available for analysis only the copper content was determined. The analysis was performed by means of electrolysis<sup>11</sup> and the copper content was found to be 43.9 %, which is in fair agreement with the calculated copper content of Cu(N<sub>3</sub>)<sub>2</sub> (43.1 %). The structure determination moreover confirms that Cu(N<sub>3</sub>)<sub>2</sub> is the true formula of the product prepared.

### STRUCTURE INVESTIGATION

*X-Ray methods.* Crystals of Cu(N<sub>3</sub>)<sub>2</sub> are needle-shaped, the needle-axis being parallel to the crystallographic *b*-axis. Single crystals were therefore rotated about the needle-axis, and multiple film equi-inclination Weissenberg photographs were registered for four zones (*h*0*l*—*h*3*l*) using CuK $\alpha$ -radiation. The third layer line proved to be somewhat difficult to record, owing to the short crystallographic *b*-axis (3.084 Å). It was, however, important to record as many zones as possible about the *b*-axis, since, as will be apparent later, the positions of the atoms in the *y*-direction are parameter-free, and rotation about the *b*-axis thus yields the most valuable information concerning the structure.

In order to obtain accurate values for the dimensions of the unit cell, X-ray powder photographs of Cu(N<sub>3</sub>)<sub>2</sub> were taken in a Guinier focusing camera, employing CuK $\alpha$ <sub>1</sub> radiation and Pb(NO<sub>3</sub>)<sub>2</sub> (*a* = 7.8564 Å<sup>13</sup>) as an internal standard. Owing to the explosive properties of the sample, extremely small quantities were pulverised under ethanol and transferred while still moist to the sample holder of the Guinier camera.

*Unit cell and space group.* The crystals were found to have orthorhombic symmetry with a unit cell of the following dimensions, as determined from the Guinier photographs, using the Algol Programme Xalg Powder:<sup>12</sup>

*a* = 13.481 ± 0.002 Å, *b* = 3.084 ± 0.001 Å, *c* = 9.076 ± 0.002 Å, and *V* = 377.3 Å<sup>3</sup>.

Observed and calculated sin<sup>2</sup> $\theta$ -values are given in Table 1, together with observed and calculated intensities.

The density of the crystals, as determined by the flotation method, was found to be 2.59 g/cm<sup>3</sup>. The unit cell thus contains four formula units ( $\rho_{\text{calc.}} = 2.60 \text{ g/cm}^3$ ).

Table 1. X-Ray powder diffraction data for  $\text{Cu}(\text{N}_3)_2$ . Guinier camera,  $\text{CuK}\alpha_1$  radiation.

$hkl$	$10^6 \sin^2 \theta_{\text{obs}}$	$10^6 \sin^2 \theta_{\text{calc}}$	$I_{\text{obs}}$	$I_{\text{calc}}$
101	10478	10467	st	546
200	13098	13059	w	29
201	20197	20261	m	63
102	32074	32073	w	12
301	36556	36584	w	20
202	41864	41867	w	12
400	52306	52235	vw	9
302	58271	58190	m	148
011	69607	69586	vw	4
210	75410	75443	m	73
203	77891	77877	w	55
402	81086	81043	w	17
211	82688	82645	w	28
501	88710	88819	w	20
112	94448	94457	w	26
311	98858	98968	m	58
410	114635	114619	w	14
403	117063	117053	w	10
411	121825	121821	w	12
013	127165	127203	w	34
412	143375	143427	vw	6
512	172824	172809	w	26
711	229580	229555	vw	11
020	249575	249537	w	10
121	260001	260004	vw	4
322	307717	307728	vw	8

st = strong, m = medium, w = weak, vw = very weak.

It was obvious from the X-ray photographs that the following conditions of reflection were obeyed:

$hkl$ : no conditions

$Ok\bar{l}$ :  $k + l = 2n$

$h0l$ : no conditions

$hk0$ :  $h = 2n$

This is characteristic for the space groups  $Pn2_1a$  (No. 33)\* and  $Pnma$  (No. 62).<sup>13</sup>

*Determination and refinement of the structure.* The intensities of the reflexions recorded were estimated visually by comparison with a standard scale. The values obtained were corrected for Lorentz and polarisation effects, but no correction was applied for absorption, since  $\mu R$  was of the magnitude of 0.03.

The structure investigation was commenced assuming that  $Pn2_1a$  was the correct space group, since this contains  $Pnma$  as a special case.

A two-dimensional Patterson summation, based on the  $h0l$ -reflexions was undertaken. The largest peaks observed could be explained by assuming that Cu is situated in the fourfold position (4a) with the parameters  $x_{\text{Cu}} \approx 0.60$ ,

\* Orientation differing from that given in the *International Tables*.<sup>13</sup>

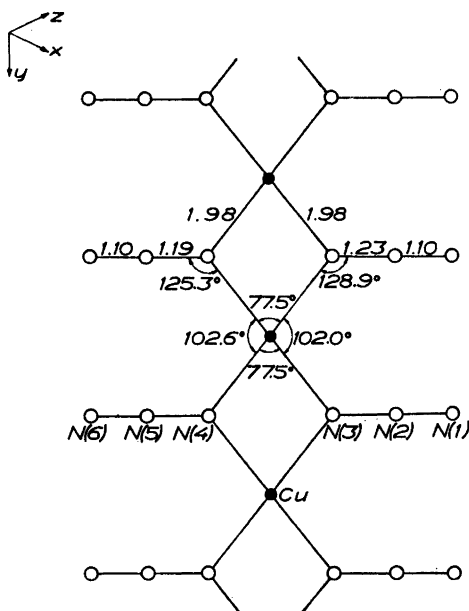


Fig. 1. A section parallel to the  $b$ -axis through the copper atoms and the connected azide groups. All atoms lie close to the plane of the paper.

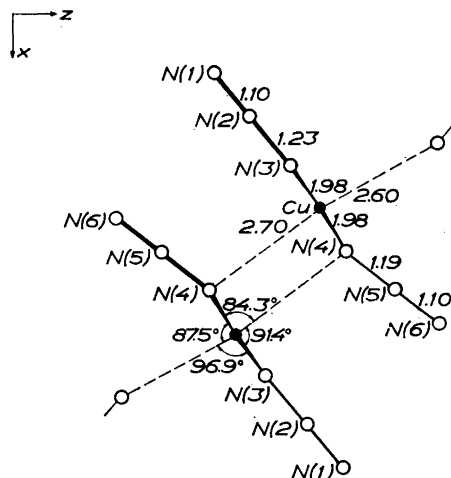


Fig. 2. Projection along the  $b$ -axis of two units of  $\text{Cu}(\text{N}_3)_2$ . The longer bond distances in the octahedra are denoted by - - - -.

$z_{\text{Cu}} \approx 0.40$ . The  $y$ -value for the first atom may be chosen at random in the space group  $Pn2_1a$ , and  $y_{\text{Cu}}$  was thus assigned the value  $y_{\text{Cu}} = 0.750$ . The approximate positions of the nitrogen atoms were found from repeated three-dimensional Fourier syntheses, from which the position of the copper atom could also be improved. The calculations indicated that all atoms were situated in planes perpendicular to the  $b$ -axis, the planes being separated by a distance of one half the length of the  $b$ -axis. It seemed therefore likely that the structure was centrosymmetrical with the atoms occupying the  $4c$  positions in the space group  $Pnma$ .

A least squares refinement based on these assumptions was then undertaken. All atoms were refined isotropically using the reflexion material then available, namely reflexion data from three zones ( $h0l-h2l$ ). The temperature coefficient of one of the nitrogen atoms (N(6), see Fig. 2) attained a higher value than those of the others, and the standard deviations were also a little larger for this atom. One explanation for this behaviour could have been that the  $y$ -coordinate of N(6) ought not to be fixed, *i.e.* that this nitrogen atom broke the centrosymmetry. That this was not the case was, however, revealed by computing a number of cycles of refinement in which the  $y$ -coordinate of N(6) was allowed to vary, *i.e.* again employing space group  $Pn2_1a$ . The temperature coefficient of N(6) did not decrease, and the best correlation between observed and calculated intensities was obtained nearest to, and on either side of, the

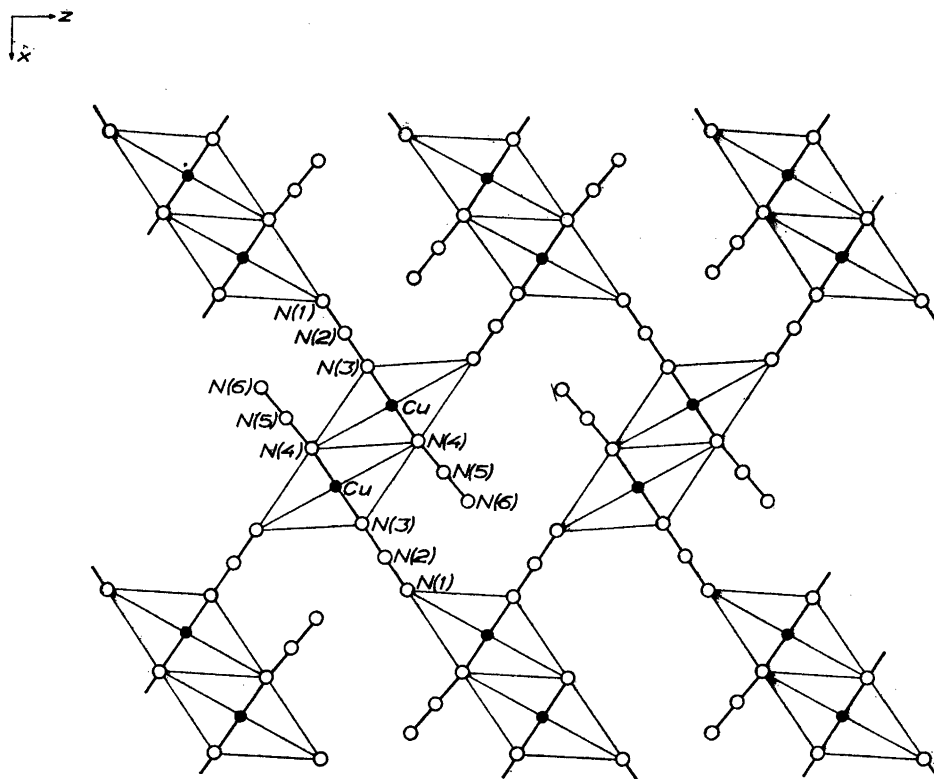


Fig. 3. Extension of the projection along the  $b$ -axis. For the sake of clarity the polyhedra have been somewhat idealized (cf. Fig. 2).

centrosymmetric position, the centrosymmetric position being included in  $y \pm \sigma_y$ . The refinement was therefore resumed according to  $Pnma$  and all atoms were refined anisotropically. The standard deviations dropped and the  $R$ -value converged to 0.058. Although too much weight should not be attached to anisotropic data, it was remarkable that the above-mentioned nitrogen atom appeared to vibrate very strongly in the  $xz$ -plane, but very little in the  $y$ -direction. This would not have been the case if the  $y$ -coordinate was incorrect, which supports the conclusion that the  $y$ -coordinate of this nitrogen atom is fixed ( $y = 0.250$ ). The strong vibration of this atom may well be explained, as is seen later on, by its structural environment, since it is the only atom which is bonded in one direction only (see Fig. 3). All other atoms are coordinated in at least two directions.

At this stage the third layer reflexions were available and were included in the reflexion material. They proved to be of great value in contributing to a more exact determination of the positions of the atoms, which was shown by the lowering of the standard deviations in the final cycles of refinement.

The final cycles of refinement were thus performed with the complete reflexion material (191 independent reflexions from four zones). When all atoms were refined anisotropically it was found that two of the nitrogen atoms (N(3) and N(2), see Fig. 2) vibrated almost spherically. In order therefore to decrease the number of parameters to be refined, these two atoms were refined isotropically, while the remaining atoms were refined anisotropically. This yielded the lowest standard deviations and a reliability index of 0.063. A three-dimensional difference synthesis computed at this stage showed no spurious peaks. The atomic coordinates and temperature coefficients are given in Table 2, and observed and calculated structure factors in Table 3.

The Lorentz and polarisation correction, the Patterson synthesis, the structure factor calculations, the Fourier syntheses, and the least squares refinement were performed on a SAAB D21 computer, using programmes written by Abrahamsson *et al.*<sup>14-17</sup> Bond distances and angles were calculated on an IBM 360/50 computer, using the programme DISTAN written by Zalkin and modified by Lundgren and Liminga.<sup>18</sup> All computer calculations were performed at the University Computing Centre in Göteborg.

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A section parallel to the *b*-axis through the copper atoms and the connected azide groups is reproduced in Fig. 1. These atoms lie almost in the same plane. Fig. 2 shows a projection along the *b*-axis of two units of the compound  $\text{Cu}(\text{N}_3)_2$ . An extension of this projection is to be found in Fig. 3. Figs. 4 and

Table 2. Atomic coordinates (expressed as fractions of the cell edges) with their standard deviations,  $\sigma$ , and thermal parameters for  $\text{Cu}(\text{N}_3)_2$ . Space group *Pnma*. Four formula units in the cell.

Atom	Position					$\sigma_z$
	<i>x</i>	<i>y</i>	<i>z</i>	$\sigma_x$	$\sigma_y$	
Cu	0.60308	0.75000	0.41978	0.00017		0.00027
N(1)	0.81158	0.25000	0.66343	0.00102		0.00167
N(2)	0.74650	0.25000	0.59084	0.00098		0.00159
N(3)	0.67670	0.25000	0.50317	0.00089		0.00136
N(4)	0.52408	0.25000	0.35102	0.00081		0.00132
N(5)	0.47071	0.25000	0.24672	0.00112		0.00180
N(6)	0.42026	0.25000	0.15152	0.00172		0.00257
Anisotropic thermal parameters						
	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{31}$	$U_{12}$
Cu	0.06780	0.07181	0.08653	0.00000	-0.00466	0.00000
N(1)	0.06495	0.08041	0.11213	0.00000	-0.04739	0.00000
N(4)	0.03317	0.09807	0.03622	0.00000	-0.00560	0.00000
N(5)	0.08596	0.05462	0.06559	0.00000	-0.01891	0.00000
N(6)	0.21583	0.06270	0.17887	0.00000	-0.11440	0.00000
Isotropic thermal parameter						
N(2)	4.525					
N(3)	4.386					

Table 3. Observed and calculated structure factors for  $\text{Cu}(\text{N}_3)_2$ . Arbitrary units.

$h k l$	$ F_o $	$ F_c $	$h k l$	$ F_o $	$ F_c $
2 0 0	2796	3062	2 0 6	837	883
4 0 0	3424	3745	4 0 6	1631	1765
6 0 0	3345	3564	6 0 6	2904	2797
8 0 0	1685	1782	8 0 6	1632	1643
10 0 0	2931	3126	10 0 6	952	678
14 0 0	2013	2019	1 0 7	1089	1080
1 0 1	7904	8308	3 0 7	935	1021
2 0 1	4274	4239	5 0 7	2528	2420
3 0 1	3576	3331	6 0 7	1154	1162
4 0 1	775	558	9 0 7	1017	793
5 0 1	4908	5060	3 0 8	1157	1053
6 0 1	1400	1632	2 0 9	1125	933
8 0 1	1493	1792	2 1 0	9360	9020
9 0 1	2828	2987	4 1 0	5211	4904
11 0 1	1555	1592	6 1 0	3576	3460
12 0 1	1059	1490	8 1 0	4059	4118
15 0 1	973	1054	12 1 0	1503	1572
0 0 2	3872	3804	0 1 1	1561	1932
1 0 2	2123	2230	2 1 1	4234	4162
2 0 2	2595	2667	3 1 1	6746	6752
3 0 2	12573	11297	4 1 1	3427	3403
4 0 2	4794	4615	5 1 1	1032	1208
6 0 2	2399	2539	6 1 1	2149	2319
7 0 2	3501	3468	7 1 1	4762	4890
9 0 2	859	785	9 1 1	1172	1477
10 0 2	1088	1226	10 1 1	1111	1298
11 0 2	2307	2304	11 1 1	1371	1486
13 0 2	1039	1075	1 1 2	4404	4414
1 0 3	1317	1268	2 1 2	1044	1271
2 0 3	8413	8103	3 1 2	2113	2114
3 0 3	4211	4131	4 1 2	2837	2767
4 0 3	4519	4360	5 1 2	7144	6355
6 0 3	3095	3088	6 1 2	2774	2762
7 0 3	849	1067	7 1 2	930	1107
8 0 3	2302	2361	8 1 2	2054	2058
12 0 3	2229	2048	9 1 2	2393	2383
0 0 4	3661	3554	0 1 3	8204	8412
1 0 4	2581	2781	2 1 3	833	877
2 0 4	696	674	3 1 3	1051	1200
3 0 4	4597	4687	4 1 3	3541	3415
4 0 4	1148	1139	5 1 3	1210	1358
5 0 4	1505	1532	6 1 3	3759	3418
6 0 4	2087	2198	8 1 3	1913	1934
7 0 4	2850	2666	10 1 3	1807	1557
8 0 4	1153	1305	14 1 3	1233	1050
9 0 4	1981	2047	1 1 4	4095	4110
11 0 4	1262	1235	2 1 4	2813	2906
1 0 5	2829	2917	3 1 4	1400	1593
2 0 5	1703	1807	5 1 4	2531	2404
3 0 5	985	806	6 1 4	1572	1556
4 0 5	1293	1294	8 1 4	1346	1318
5 0 5	2958	3174	9 1 4	1816	1610
6 0 5	2475	2556	11 1 4	1250	852
8 0 5	2579	2429	0 1 5	2352	2531
9 0 5	2430	2253	1 1 5	1967	2151
0 0 6	2872	2831	2 1 5	861	976

Table 3. Continued.

<i>h k l</i>	$ F_o $	$ F_c $	<i>h k l</i>	$ F_o $	$ F_c $
3 1 5	3037	3045	5 2 5	1302	1379
4 1 5	1274	1365	6 2 5	976	1045
5 1 5	1213	1288	8 2 5	1065	1055
6 1 5	1527	1618	9 2 5	962	1056
7 1 5	1116	1069	0 2 6	1143	1322
11 1 5	1203	1034	6 2 6	1273	1231
2 1 6	2665	2975	5 2 7	1224	1089
4 1 6	1547	1551	2 3 0	1386	1519
12 1 6	1112	939	4 3 0	985	1019
1 1 7	1231	1409	6 3 0	742	580
3 1 7	2053	2014	8 3 0	694	735
1 1 8	1194	1187	2 3 1	403	523
0 1 9	1423	1431	3 3 1	1534	1202
2 2 0	1030	1029	4 3 1	748	550
4 2 0	1975	1912	6 3 1	497	428
6 2 0	1684	1646	7 3 1	880	900
10 2 0	1295	1326	9 3 1	242	279
1 2 1	2749	2939	1 3 2	749	918
2 2 1	1763	1536	2 3 2	353	237
3 2 1	1365	1422	3 3 2	463	327
5 2 1	2288	2146	4 3 2	490	454
9 2 1	1258	1240	5 3 2	1106	1083
0 2 2	1759	1670	6 3 2	447	570
1 2 2	1013	1146	8 3 2	329	476
3 2 2	3989	3949	9 3 2	360	501
4 2 2	1810	1723	0 3 3	1424	1566
6 2 2	1265	998	4 3 3	670	562
7 2 2	1537	1512	6 3 3	636	656
11 2 2	1010	1009	8 3 3	313	441
2 2 3	3140	3140	1 3 4	721	700
3 2 3	1059	1201	2 3 4	471	564
4 2 3	1679	1712	3 3 4	289	326
6 2 3	1076	1293	5 3 4	549	496
8 2 3	1367	1025	6 3 4	254	295
0 2 4	1049	1199	0 3 5	373	419
1 2 4	969	1125	1 3 5	342	416
3 2 4	1863	1985	3 3 5	553	624
7 2 4	1057	1095	4 3 5	233	344
1 2 5	1078	1198	2 3 6	472	630
2 2 5	840	819			

5 illustrate from different points of view how the structure is built up by the linking of distorted octahedra. Atomic distances and angles are given in Tables 4 and 5.

The copper atom is surrounded by four nitrogen atoms in an elongated square-planar configuration, the edges of the rectangle being  $3.084 \pm 0.001$  Å and  $2.478 \pm 0.017$  Å. The distances from the central copper atom to the nitrogen atoms have been determined to be  $1.975 \pm 0.007$  Å and  $1.984 \pm 0.008$  Å. These values are in agreement with copper-nitrogen distances found in other structures, where the distances lie close to 2 Å.<sup>20</sup> In  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$  the corresponding distances were found to be  $2.053 \pm 0.008$  Å and  $2.052 \pm 0.008$  Å.<sup>10</sup>



**Table 4.** Interatomic distances in  $\text{Cu}(\text{N}_3)_2$  with their standard deviations,  $\sigma$ . The numbers enclosed in square brackets indicate atomic coordinates.

	Distance (Å)	$\sigma$ (Å)
a) Cu—N distances within the coordination sphere:		
Cu [0.3969, 0.2500, 0.5802] — N(3) [0.3233, 0.7500, 0.4968]	1.984	0.008
Cu [0.3969, 0.2500, 0.5802] — N(4) [0.4759, 0.7500, 0.6490]	1.975	0.007
Cu [0.3969, 0.2500, 0.5802] — N(1) [0.3116, 0.2500, 0.8366]	2.596	0.015
Cu [0.3969, 0.2500, 0.5802] — N(4) [0.5241, 0.2500, 0.3510]	2.696	0.012
b) N—N distances within the azide groups:		
N(1) [0.8116, 0.2500, 0.6634] — N(2) [0.7465, 0.2500, 0.5908]	1.097	0.020
N(2) [0.7465, 0.2500, 0.5908] — N(3) [0.6767, 0.2500, 0.5032]	1.232	0.018
N(1) [0.8116, 0.2500, 0.6634] — N(3) [0.6767, 0.2500, 0.5032]	2.328	0.019
N(4) [0.5241, 0.2500, 0.3510] — N(5) [0.4707, 0.2500, 0.2467]	1.189	0.020
N(5) [0.4707, 0.2500, 0.2467] — N(6) [0.4203, 0.2500, 0.1515]	1.100	0.028
N(4) [0.5241, 0.2500, 0.3510] — N(6) [0.4203, 0.2500, 0.1515]	2.289	0.026
c) Selected distances other than bond distances:		
Cu [0.3969, 0.2500, 0.5802] — Cu [0.3969, 1.2500, 0.5802]	3.084	0.001
Cu [0.3969, 0.2500, 0.5802] — Cu [0.6031, 0.7500, 0.4198]	3.496	0.004
N(3) [0.6767, 0.2500, 0.5032] — N(4) [0.5241, 0.2500, 0.3510]	2.478	0.017
N(3) [0.6767, 0.2500, 0.5032] — N(3) [0.6767, 1.2500, 0.5032]	3.084	0.001

**Table 5.** Angles in  $\text{Cu}(\text{N}_3)_2$ . Notation as in Table 4.

	Angle (°)	$\sigma$ (°)
a) N—Cu—N and Cu—N—N angles within the coordination sphere:		
N(1) [0.312, 0.250, 0.837] — Cu [0.397, 0.250, 0.580] — N(3) [0.323, 0.750, 0.497]	96.9	0.4
N(1) [0.312, 0.250, 0.837] — Cu [0.397, 0.250, 0.580] — N(4) [0.476, 0.750, 0.649]	87.5	0.4
N(3) [0.323, 0.750, 0.497] — Cu [0.397, 0.250, 0.580] — N(4) [0.524, 0.351, 0.250]	91.4	0.4
N(4) [0.524, 0.250, 0.351] — Cu [0.397, 0.250, 0.580] — N(4) [0.476, 0.750, 0.649]	84.3	0.4
N(3) [0.323, 0.750, 0.497] — Cu [0.397, 1.250, 0.580] — N(3) [0.323, 1.750, 0.497]	102.0	0.6
N(4) [0.476, 0.750, 0.649] — Cu [0.397, 1.250, 0.580] — N(4) [0.476, 1.750, 0.649]	102.6	0.5
N(3) [0.323, 0.750, 0.497] — Cu [0.397, 0.250, 0.580] — N(4) [0.476, 0.750, 0.649]	77.5	0.4
Cu [0.603, 0.750, 0.420] — N(3) [0.677, 0.250, 0.503] — N(2) [0.746, 0.250, 0.591]	128.9	0.3
Cu [0.603, 0.750, 0.420] — N(4) [0.524, 0.250, 0.351] — N(5) [0.471, 0.250, 0.247]	125.3	0.4
b) N—N—N angles within the azide groups:		
N(1) [0.812, 0.250, 0.663] — N(2) [0.746, 0.250, 0.591] — N(3) [0.677, 0.250, 0.503]	176.7	1.7
N(4) [0.524, 0.250, 0.351] — N(5) [0.471, 0.250, 0.247] — N(6) [0.420, 0.250, 0.152]	179.0	2.1
c) Selected angles other than bond angles:		
Cu [0.897, 0.250, 0.920] — N(1) [0.812, 0.250, 0.663] — N(2) [0.746, 0.250, 0.591]	153.2	1.3
N(2) [0.746, 0.250, 0.591] — N(3) [0.677, 0.250, 0.503] — N(4) [0.524, 0.250, 0.351]	173.7	1.1
N(3) [0.677, 0.250, 0.503] — N(4) [0.524, 0.250, 0.351] — N(5) [0.471, 0.250, 0.247]	161.1	1.1

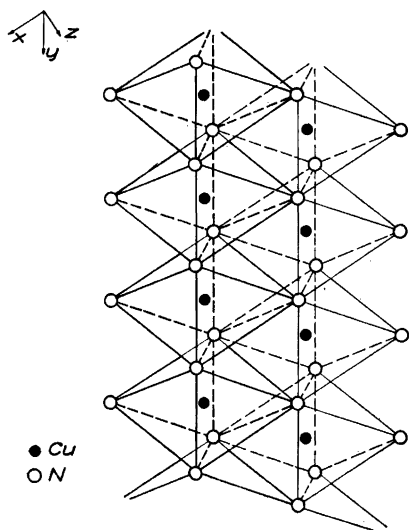


Fig. 4. A double chain of octahedra stretching along the  $y$ -axis. The azide groups are not indicated but are directed away from the corners of the square in the octahedra perpendicular to the  $y$ -axis as well as to the direction of the longer octahedra distances (*cf.* Fig. 1).

As expected, due to the Jahn-Teller effect,<sup>19</sup> the copper atom is distorted octahedrally coordinated, having, besides the four nearest neighbours, two further neighbouring nitrogen atoms at somewhat longer distances. The longer copper-nitrogen distances in  $\text{Cu}(\text{N}_3)_2$  were found to be  $2.596 \pm 0.015 \text{ \AA}$  and  $2.696 \pm 0.012 \text{ \AA}$ . In  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$  the corresponding distances were found to be  $2.56 \pm 0.01 \text{ \AA}$  and  $2.67 \pm 0.01 \text{ \AA}$ .<sup>10</sup> The structure can be visualised as being built up of octahedra closely linked together by the sharing of edges to form a double chain (Fig. 4). These chains stretch parallel to the  $b$ -axis, and are, in their turn, joined together by azide groups lying in planes perpendicular to the  $b$ -axis (Fig. 5). There is a resemblance between the structure of  $\text{Cu}(\text{N}_3)_2$  and that of, for example,  $\text{CuCl}_2$ ,<sup>22</sup> which is obvious when considering, for instance, Fig. 1. In both cases chains of octahedra are built up by the sharing of opposite edges, but the coupling of these chains is different. It is also interesting to compare the chains of octahedra in  $\text{Cu}(\text{N}_3)_2$  with those found in  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$ , in which double chains of octahedra stretch in one direction, and are joined together by weaker bonds. The coupling in  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$  is, however, different, as the octahedra in the double chains are linked together through a common corner as well as through an azide group, and the chains, in their turn, are joined by hydrogen bonding.<sup>10</sup>

The observed deviation of the four nearest neighbours of the copper atom from the expected square-planar configuration (Fig. 1) may be due to a slight repulsion between the copper atoms, the distance between these crystallographically identical copper atoms being  $3.084 \pm 0.001 \text{ \AA}$ . The remaining copper atoms within the double chains also appear to repel each other, resulting in a displacement of the copper atoms from the centres of the octahedra (Fig. 2). The distance between these copper atoms is calculated to be  $3.496 \pm 0.004 \text{ \AA}$ . Since the copper-copper distance in metallic copper is

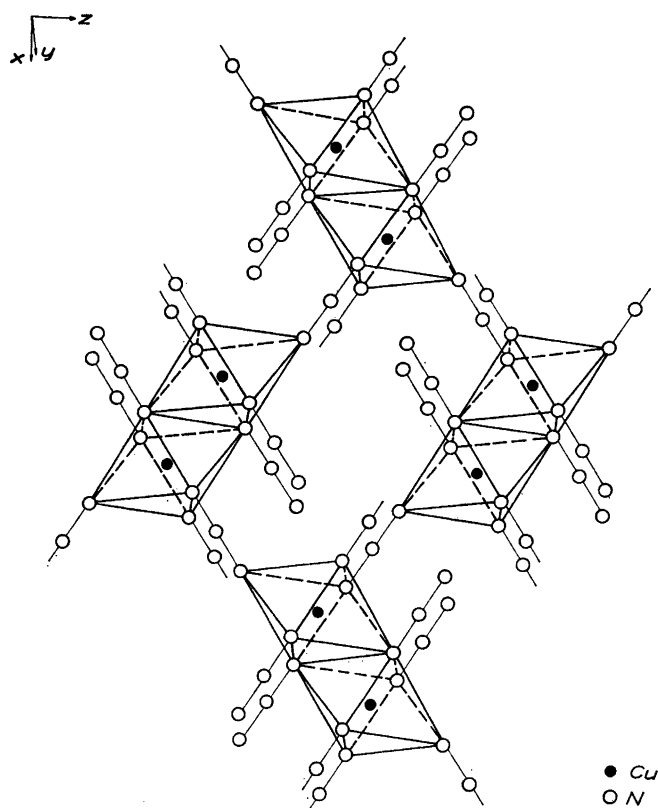


Fig. 5. The packing of the chains of octahedra as viewed perpendicular to the  $xz$ -plane.

2.556 Å,<sup>20</sup> the bonding forces in the structure cannot be attributed to Cu—Cu interaction.

The nitrogen-nitrogen distances within the azide group, N(3)—N(2)—N(1) (Fig. 1), have been determined to be  $1.232 \pm 0.018$  Å and  $1.097 \pm 0.020$  Å, and within the other azide group, N(4)—N(5)—N(6), to be  $1.189 \pm 0.020$  Å and  $1.100 \pm 0.028$  Å. In both cases, the longest N—N distance is closest to the Cu—N bond. The N—N distances within both azide groups are of different lengths, thus confirming the asymmetry of the azide groups. Both azide groups are found to be linear within experimental error ( $176.7 \pm 1.7^\circ$  and  $179.0 \pm 2.1^\circ$ ). The angle between the azide group N(1)—N(2)—N(3) and the Cu—N bond is  $128.9 \pm 0.3$  Å and that between the azide group N(4)—N(5)—N(6) and the Cu—N bond is  $125.3 \pm 0.4$  Å. This may be compared with, for instance, the organic asymmetric azide  $\text{CH}_3\text{N}_3$ , where the distances are reported to be 1.24 Å and 1.10 Å and the angle to be  $120 \pm 5^\circ$ .<sup>21</sup> The N—N bond distances may also be compared with the values found in  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$ ,<sup>10</sup> where the longer N—N distances in the two azide groups were found to be  $1.174 \pm 0.011$  Å and  $1.186 \pm 0.011$  Å, respectively, and the

shorter N—N distances to be  $1.142 \pm 0.012 \text{ \AA}$  and  $1.139 \pm 0.013 \text{ \AA}$ . The corresponding angles were  $116.3 \pm 0.5^\circ$  and  $121.4 \pm 0.5^\circ$ , respectively, in  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]^{10}$ .

The coordination of the two azide groups in  $\text{Cu}(\text{N}_3)_2$  is not the same. The azide group N(1)—N(2)—N(3) is bonded through N(3) to two identical copper atoms at a short distance of 1.984 Å and through N(1) to another copper atom at a longer distance of 2.596 Å. The azide group is thus coordinated at both ends, and it is through this azide group that the double chains are connected to form a three-dimensional net (Fig. 3). The other azide group, N(4)—N(5)—N(6), is bonded at one end only, namely, through N(4) to two identical copper atoms at a short distance of 1.975 Å and also through N(4) to another copper atom at a longer distance of 2.696 Å. This azide group is directed away from the octahedral chains (Fig. 3) and the end nitrogen, N(6), is unique, in that it is the only atom coordinated in one direction only, which seems to result in a greater vibration of this atom than of the remaining atoms in the structure.

*Acknowledgements.* I would like to thank Professor Cyrill Brosset for his interest in the subject. I also wish to express my gratitude to Professor Georg Lundgren and to Docent Nils-Gösta Vannerberg for their encouragement and helpful discussions. I am indebted to Mrs. Margareta Biéth for her skilful technical assistance, to Ing. Ingrid Ingvarsson for drawing the figures and to Fil.lic. Susan Jagner for correcting the English text of this paper.

#### REFERENCES

1. Curtius, T. and Rissom, J. *J. prakt. Chem.* [2] **58** (1898) 261.
2. Straumanis, M. and Cirulis, A. *Z. anorg. Chem.* **251** (1943) 315.
3. Evans, B. L. and Yoffe, A. D. *Proc. Roy. Soc. (London)* **A 238** (1957) 568.
4. Evans, B. L. *Proc. Roy. Soc. (London)* **A 246** (1958) 199.
5. Deb, S. K. and Yoffe, A. D. *Proc. Roy. Soc. (London)* **A 256** (1960) 528.
6. Lamnevik, S. *Prevention of copper azide formation in ammunition, Copper azide corrosion*, mimeographed and distributed at the Symposium on Azides in London, Oct. 1966.
7. Gray, P. *Quart. Rev. (London)* **17** 4 (1963) 441.
8. Ohkubo, S., Shiino, K. and Oinuma, S. *Rept. Gov. Chem. Ind. Res. Inst. Tokyo*. **52** (1957) Sept.
9. Palenik, G. J. *Acta Cryst.* **17** (1964) 360.
10. Agrell, I. *Acta Chem. Scand.* **20** (1966) 1281.
11. Kolthoff, I. M. and Sandell, E. B. *Textbook of Quant. Inorg. Analysis*, 3rd Ed., The Macmillan Co., (1952) 408.
12. Lindqvist, O. and Wengelin, F. *Private communication*.
13. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1959.
14. Abrahamsson, S. and Larsson, K. *Arkiv Kemi* **24** (1965) 383.
15. Abrahamsson, S. *Arkiv Kemi* **24** (1965) 389.
16. Aleby, S. *Arkiv Kemi* **24** (1965) 395.
17. Larsson, K. *Arkiv Kemi* **23** (1964) 17.
18. Zalkin, et al. *Private communication*.
19. Orgel, L. E. *An Introduction to Transition Metal Chemistry: Ligand Field Theory*, Methuen 1960, 57.
20. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London 1958, Suppl. 1956—1959.
21. Pauling, L. and Brockway, L. O. *J. Am. Chem. Soc.* **59** (1937) 13.
22. Wells, A. F. *Structural Inorganic Chemistry*, The Clarendon Press, Oxford 1962, p. 347.

Received June 22, 1967.