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Studies on Explosives
I. The Crystal Structure of Copper(II) Azide, Catena-diazidocopper(II)

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The crystal structure of orthorhombic copper(II) azide has been determined by single-crystal X-ray diffraction methods using complete, visually estimated, intensity data within the Cu $K\alpha$ sphere and with space group *Pbnm*. The refined lattice parameters are at 25°C $a=9{\cdot}084\pm0{\cdot}003$, $b=13{\cdot}454\pm0{\cdot}002$, $c=3{\cdot}079\pm0{\cdot}001$ Å and the unit cell contains four $Cu(N_3)_2$. The trial structure was refined by the method of full-matrix least-squares to a final residual of 0·059. The structure consists of planar diazidocopper(II), $[Cu(N_3)_2]_n$, chain molecules packed laterally with long Cu–N distances and distorted octahedral coordination around each copper atom. The Cu–N distances are close to 2·00 Å within the chains and the N–N bonds in the azido groups are found to differ significantly in length.

Introduction

Copper(II) azide, $Cu(N_3)_2$, was first prepared by Curtius & Rissom (1898) and the lattice parameters were determined by Straumanis & Cirulis (1943). At the Research Institute of National Defence (FOA) in Sweden the system $Cu(N_3)_2$–CuO–H_2O has been investigated by Lamnevik & Söderquist (1967). Several of the solid phases in this system are explosive corrosion products formed on copper and copper alloys at various partial pressures of hydrogen azide. Copper(II) azide is the stable compound at partial pressures higher than 0·24 torr at 25°C, whereas at lower partial pressures hydrolysis to hydroxo compounds of $Cu(N_3)_2$ occurs.

Copper(II) azide is a primary explosive, extremely sensitive to impact, friction and, especially, electrical fields. The electrical sensitivity is so high that the compound will detonate at discharge energies in the microjoule range (Lamnevik, 1966). This indicates that the compound has small activation energies for thermal and electrical breakdown which may be related to the crystal structure. The extreme sensitivity of $Cu(N_3)_2$ seems, however, not to be caused by a polarity of the crystals as suggested for many other explosives by Maycock & Grabenstein (1966).

Experimental

Crystals of copper(II) azide suitable for single-crystal optical and X-ray work were prepared by two different methods, either according to Straumanis & Cirulis (1943) or by a diffusion method. In the latter method $CuSO_4.5H_2O(s)$ and $NaN_3(s)$ contained in small beakers were allowed to mix by diffusion in a solution of 1% hydrogen acetate in water. Both preparation methods gave long prismatic greenish black needles, which analysed as $Cu(N_3)_2$, Cu: $42{\cdot}9_2\%$ (calc. 43·06%) from ethylenediaminetetra-acetate titrations, and N: $56{\cdot}4_3\%$ (calc. 56·94%) from Ce^{IV} titrations.

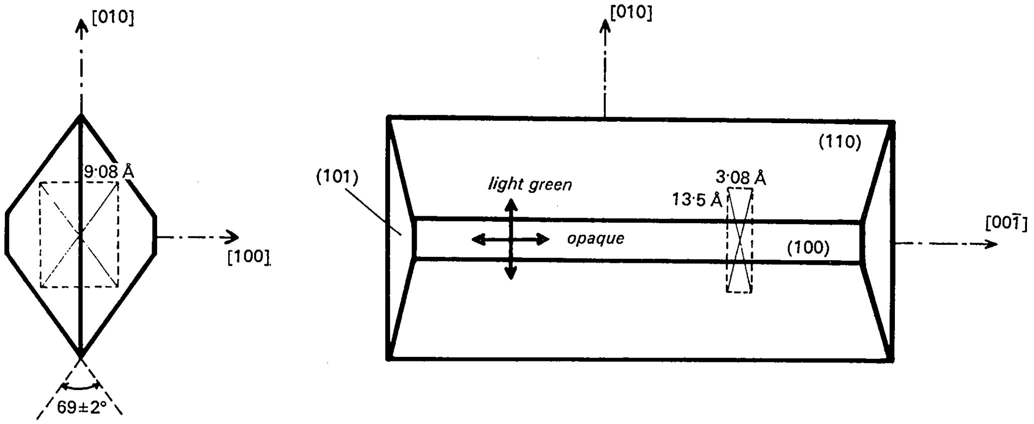

Fig. 1. Orthographic projections of the common habit of well-crystallized orthorhombic $Cu(N_3)_2$. The unit cell and pleochroism are indicated.

The crystals are stable in air and mostly grow with a few well-developed faces of holohedral symmetry (Fig. 1). Occasionally minute faces and striations along [001] occur which probably prevented Straumanis & Cirulis (1943) from identifying the main crystal forms. There are also perfect cleavages along the needle axis which cause the crystals to split at the slightest pressure into a bundle of thin fibres looking much like asbestos. $Cu(N_3)_2$ shows extremely strong pleochroism, being opaque along [001] but transparent with light green transmission in the (001) plane. This property explains to some extent the diversity in the description of the colour of this compound, ranging from green or brown to black.

The X-ray pattern obtained from $Cu(N_3)_2$ has *mmm* symmetry, and the orientation of the unit-cell axes within the crystal is shown in Fig. 1. The lattice parameters (Table 1) confirm those given by Straumanis & Cirulis (1943) and 32 single-indexed diffraction lines were refined by the method of least-squares (unit weights) using powder data obtained with a Hägg–Guinier focusing camera (Table 2). 408 of a total of 526 recorded independent intensities (96% of all possible within the Cu $K\alpha$ sphere) were above background and measured by visual comparison with calibrated scales from non-integrated Weissenberg equi-inclination ($\mu_{\max} = 30°$) multiple-films taken around all three principal axes (*nkl*, $n = 0$–5; *hnl*, $n = 0$–2; *hkn*, $n = 0$–2).

Table 1. *Some crystal data on orthorhombic* $Cu(N_3)_2$ *at* 25 °C

Cell constants

$a \pm \sigma = 9{\cdot}084 \pm 0{\cdot}003$ Å
$b \pm \sigma = 13{\cdot}454 \pm 0{\cdot}002$
$c \pm \sigma = 3{\cdot}079 \pm 0{\cdot}001$
$V \pm \sigma = 376{\cdot}3 \pm 0{\cdot}3$ Å^3

Densities

$\varrho_o = 2{\cdot}58$ g.cm^{-3} (flotation in 1-bromonaphthalene–diiodomethane mixtures)
$\varrho_c = 2{\cdot}604$ g.cm^{-3}, $Z = 4$ $Cu(N_3)_2$, $Cu(N_3)_2 = 147{\cdot}6$ g.mole^{-1}.

Diffraction data

$\mu = 70{\cdot}5$ cm^{-1} (Cu $K\alpha$)
$F(000) = 284$ electrons

Observed reflexions:		
	hkl	no conditions
	0*kl*	$k = 2n$
	*h*0*l*	$h + l = 2n$
	*hk*0	no conditions

Space groups: *Pbnm* (no. 62, 010/001/100 transforms to standard setting)
$Pbn2_1$ (no. 33, 010/100/00$\bar{1}$ transforms to standard setting)

Crystal morphology

Orthorhombic holohedral
$a:b:c = 0{\cdot}6752:1:0{\cdot}2289$
Perfect cleavage along [001]

Crystal optics

Strong pleochroism, opaque along [001], light green in (001)

Piezoelectricity

Negative (static and Giebe & Scheibe method)

Table 2. *X-ray powder diffraction data of orthorhombic* $Cu(N_3)_2$

Hägg–Guinier focusing camera (80 mm diameter, quartz monochromator) with λ (Cu$K\alpha_1$) = 1·54051 Å radiation and KCl ($a = 6{\cdot}29294$ Å at 25 °C) as internal standard.

d_o (Å)	I_{rel}	*hkl*	d_o^{-2} (Å^{-2})	d_c^{-2} (Å^{-2})
7·524	*vs*	110	0·01766	0·01765
6·725	*w*	020	0·02211	0·02210
5·406	*m*	120	0·03422	0·03422
4·535	*vw*	200	0·04863	0·04848
4·307	*vw*	210	0·05390	0·05400
4·023	*w*	130	0·06179	0·06184
3·764	*vw*	220	0·07059	0·07057
3·365	*vw*	040	0·08830	0·08830
3·190	*s*	230	0·09823	0·09820
2·915	*vw*	101	0·11770	0·11762
2·800	*s*	021	0·12753	0·12759
2·762	*w*	320	0·13110	0·13118
2·703	*w*	240	0·13688	0·13688
2·676	*m*	121	0·13970	0·13971
2·582	*w*	150	0·15001	0·15024
2·504	*w*	211	0·15943	0·15950
2·445	*m*	131	0·16722	0·16733
2·272	*w*	041	0·19377	0·19390
		400	0·19377	0·19392
2·249	*vw*	340	0·19766	0·19747
2·203	*w*	141	0·20599	0·20602
2·160	*vw*	301	0·21433	0·21458
2·031	*vw*	241	0·24233	0·24237
2·012	*vw*	260	0·24700	0·24736
1·979	*vw*	151	0·25573	0·25574
1·851	*w*	251	0·29195	0·29220
1·802	*vw*	360	0·30808	0·30796
		510	0·30808	0·30853
1·778	*vw*	161	0·31647	0·31650
1·682	*vw*	261	0·35330	0·35286
		080	0·35330	0·35357
1·606	*w*	171	0·38789	0·38832
1·555	*vw*	361	0·41344	0·41346
		511	0·41344	0·41401
1·540	*m*	002	0·42177	0·42198
1·508	*w*	112	0·43987	0·43963
1·478	*vw*	531	0·45758	0·45820
1·387	*vw*	232	0·51973	0·52018
1·344	*vw*	322	0·55320	0·55317
1·322	*vw*	152	0·57220	0·57223

The crystals disintegrate rapidly in X-ray radiation, resulting in fading of the intensities on repeated exposure. Thus new crystals were mounted for each reciprocal layer. Corrections for the Lorentz and polarization effects were applied, and the *hk*3 reflexions were brought to the same level by cross-correlation. About 85% of the intensities were collected around [001] with rod-shaped crystals of diameters less than 0·04 mm giving a transmission correction not exceeding 5%. It was thus not considered necessary to correct all the crystals used for absorption since errors due to disintegration may exceed the absorption effect. The conditions for observed reflexions (Table 1) are in accordance with space groups $Pbn2_1$ (no. 33) and *Pbnm* (no. 62) in *International Tables for X-ray Crystallography* (1952).

Inspection of the X-ray photographs reveals that *hkl* reflexions differing only by 2*n* in *l* have nearly uniform intensity apart from the normal decline with increasing θ. This strongly suggests location of the four $Cu(N_3)_2$ units on mirror planes at $z=\pm\frac{1}{4}$, thus transforming the general fourfold position in $Pbn2_1$ to the fourfold special position with symmetry m in $Pbnm$. For this reason and because of the apparent holohedry of the crystals, space group $Pbnm$ was adopted during the structure determination. The position of the copper atom was easily deduced from the Patterson projection on (001). Two successive Fourier syntheses based on $F_{\rm rel}$ enabled the x and y coordinates of all six nitrogen atoms to be determined. The z coordinates $(\pm\frac{1}{4})$ were assigned to give reasonable Cu–N distances of about 2·0 Å and linear N_3 groups. These positions were checked on a Patterson projection on (100). A structure factor calculation at this stage, including all measured reflexions and approximate temperature factors resulted in a discrepancy index, defined throughout as

$$R=\Sigma\,\big||F_o|-|F_c|\big|/\Sigma\,|F_o|\,,$$

of 0·26.

The structure was refined by a full-matrix least-squares analysis minimizing the function $w(|F_o|-|F_c|)^2$ and using only the 408 reflexions above background. These were given unit weight for scaled $F_o\le 4F_{\rm min}=20$ electrons and for reflexions with $F_o>20$ electrons $\sqrt{w}$ was set equal to $20/F_o$. Neutral atomic scattering factors, without dispersion corrections, were taken from *International Tables for X-ray Crystallography* (1962). The calculations were carried out on an IBM 7090 computer, with a set of programs written or adapted by Stewart (1964).

The structure was first refined by six cycles in the isotropic mode when the shifts had reached $0{\cdot}01\sigma$ for all parameters and $R=0{\cdot}082$. A three-dimensional Fourier synthesis with ΔF values as amplitudes showed no evidence ($\Delta\varrho$ approximately zero around all atoms) of displacement of any of the atoms from the mirror planes as would be expected if the structure were non-centrosymmetric. In the three-dimensional electron density one of the terminal nitrogen atoms [N(6), see below] was slightly smeared in the xy plane as compared with the others, indicating stronger thermal motion. Five more cycles with individual anisotropic temperature factors applied to all atoms were calculated refining a total of 43 parameters (14 structural and 28 temperature factor parameters and one scale factor). R decreased to a final value of 0·059 and the shifts of all the parameters were negligible. A statistical test, using an approximate R-factor ratio (Hamilton, 1965), of the physical significance of introducing anisotropic refinement was definitely positive, well above the 99·5% level. Averages of $\Sigma w(|F_o|-|F_c|)^2$ in groups of increasing F_o and $\sin\theta/\lambda$ justified the weighting scheme used and minor changes in the weights produced little effect; this indicates that the errors in the data are mostly of random nature. No reflexions seemed to be affected by extinction; this may be ascribed to the fibrous mosaic structure of $Cu(N_3)_2$ proposed by Straumanis & Cirulis (1943).

Discussion

The configuration, bond lengths and angles (Fig. 2 and Table 5) of both the N_3 groups (almost linear) and the copper coordination (octahedral 4+1+1) found in $Cu(N_3)_2$ agree well with similar values in related structures (Agrell, 1966). The structure can be considered as being built from infinite, almost planar chain molecules of composition $Cu(N_3)_2$, running along [001] in the crystal. The two crystallographically independent N_3 groups in the repeat unit of a chain coordinate the copper atom by one terminal nitrogen each, the copper atom being surrounded by four N_3 ligands in a rectangular plane. The two Cu–N distances are both very

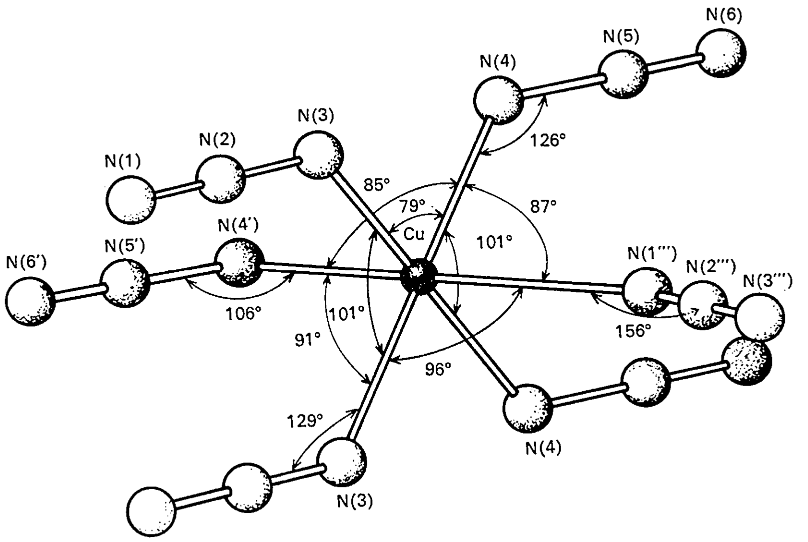

Fig. 2. Perspective view of the octahedral environment of a copper atom in $Cu(N_3)_2$.

close to 2·00 Å and the interbond angle is 79·2°. The axes of the N_3 groups are slightly turned in (001) to fall out of the coordination plane and make angles of 129·3 and 126·0° with the Cu–N bonds (Fig. 2); these values lie in the region reported for other covalently bonded azido groups. This neutral, infinite chain structure of copper(II) azide explains the fibrous cleavage. Copper(II) azide can be considered an azido complex of copper(II), $[Cu(N_3)_2]_n$, suggesting the systematic name catena-diazidocopper(II). There is a relatively short Cu–Cu distance, 3·08 Å, along the chains. Although no direct Cu–Cu bonding is proposed at such distance (Schlueter, Jacobson & Rundle, 1966), this may, however, result in an increase of the amount of light absorbed in the chain direction, suggesting an explanation of the extremely strong pleochroism observed.

The lateral packing of the chains in $Cu(N_3)_2$ conforms to the usual pattern of copper(II) compounds, forming distorted octahedral configurations around the copper atom (Wells, 1962). The two azido ligands form, apart from the short intrachain bonds with copper, one long Cu–N bond each to a neighbouring chain (Fig. 3). Both N_3 groups are thus three-coordinated to copper but in different ways. The N(1)–N(2)–N(3) group coordinates in both ends; long Cu–N(1) distances of 2·54 Å bind the chains to puckered layers in (010) consisting of five-coordinated copper pyramids. These layers are stacked together with the basal planes of the pyramids parallel and connected through Cu–N(4) bonds of 2·71 Å across the planes, completing the distorted octahedral surrounding of copper. Thus the N(4)–N(5)–N(6) group uses only N(4) in copper bonding, leaving the opposite nitrogen atom N(6) with

Table 3. *Final observed and calculated structure factors of* $Cu(N_3)_2$

The columns are, *h*, $10|F_o|$ and $10F_c$. Unobserved reflexions are marked with an asterisk and have been given F_o values corresponding to the estimated minimum observable intensity. They have been omitted from the least-squares refinement.

H,0,0		
2	413	399
4	444	-437
6	430	-424
8	142	-134
10	69	46
H,1,0		
1	819	834
2	271	-275
3	184	181
4	340	-372
5	400	-415
6	24*	-19
7	259	-247
8	132	140
9	81	-70
10	106	95
11	127	117
H,2,0		
0	329	309
1	469	-440
2	296	-282
3	807	-870
4	105	-97
5	270	-293
6	168	-150
7	115	112
8	25*	-13
9	291	287
10	109	-93
11	108	117
H,3,0		
1	344	-366
2	1209	-1235
3	442	-437
4	528	-572
5	134	137
6	25*	-9
7	181	187
8	245	253
9	144	-122
10	221	204
11	50	-66
H,4,0		
0	391	-413
1	99	78
2	489	-519
3	508	-512
4	188	204
5	205	-203
6	299	332
7	27*	47
8	173	179
9	148	146
10	91	-82
11	30	48
H,5,0		
1	507	-545
2	23*	-15
3	19*	14
4	229	218
5	418	454
6	25*	0
7	455	486
8	119	-125
9	25*	48
10	41	-48
11	54	-97
H,6,0		
0	435	-443
1	214	227
2	331	-335
3	384	395
4	318	318
5	357	355
6	474	475
7	231	-235
8	202	192
9	156	-148
10	44	-55
H,7,0		
1	19*	-37
2	460	463
3	145	-143
4	421	422
5	67	60
6	26*	63
7	122	119
8	158	-154
9	23*	-15
10	163	-165
H,8,0		
0	256	248
1	255	253
2	110	115
3	385	361
4	227	-218
5	411	404
6	290	-286
7	133	-133
8	101	-96
9	184	-177
10	14*	24
H,9,0		
1	426	437
2	153	153
3	71	-84
4	353	341
5	385	-381
6	28*	14
7	224	-219
8	125	-113
9	38	-51
H,10,0		
0	503	478
1	19*	-27
2	215	220
3	163	-155
4	177	-149
5	55	55
6	169	-173
7	25*	-7
8	143	-145
9	15*	16
H,11,0		
1	282	271
2	387	-390
3	143	138
4	245	-243
5	114	-113
6	25*	0
7	129	-118
8	117	108
H,12,0		
0	97	85
1	238	-243
2	134	120
3	393	-403
4	50	-42
5	72	-62
6	23*	1
7	25*	33
8	13*	-12
H,13,0		
1	164	-157
2	237	-215
3	26*	-36
4	137	-117
5	103	103
6	19*	-39
7	38	48
H,14,0		
0	429	-420
1	25*	-30
2	156	-143
3	80	-92
4	91	76
5	19*	-5
6	157	159
H,15,0		
1	230	-237
2	26*	-33
3	18*	-1
4	71	70
5	120	125
H,16,0		
0	91	-94
1	34	43
2	17*	-1
3	127	129
H,0,1		
1	220	223
3	937	970
5	375	393
7	126	-126
9	337	-350
11	52	-56
H,1,1		
1	41*	6
2	528	527
3	116	112
4	500	540
5	328	-336
6	84	88
7	253	-273
8	272	-268
9	51	-44
10	103	-108
11	31*	24
H,2,1		
0	984	1002
1	499	-454
2	193	169
3	127	129
4	405	-397
5	168	155
6	506	-484
7	48	-3
8	206	-212
9	112	-95
10	42*	22
11	31*	17
H,3,1		
1	703	765
2	290	-262
3	168	166
4	267	-244
5	478	-453
6	46	39
7	379	-388
8	51	36
9	47	-17
10	68	71
11	62	145
H,4,1		
0	572	577
1	450	-412
2	317	337
3	403	-435
4	66	49
5	250	-233
6	308	-274
7	75	103
8	48	-1
9	98	114
10	39*	57
H,5,1		
1	182	-163
2	768	-801
3	182	165
4	384	-380
5	194	163
6	48	1
7	50	74
8	109	118
9	44	-4
10	174	195
H,6,1		
0	459	-451
1	318	-292
2	403	-378
3	468	-472
4	262	234
5	276	-259
6	178	172
7	131	135
8	84	98
9	173	172
10	31*	-53
H,7,1		
1	593	-631
2	161	-155
3	48	6
4	78	-85
5	219	181
6	71	59
7	157	166
8	47	-8
9	42*	24
10	28*	35
H,8,1		
0	543	-549
1	75	91
2	318	-308
3	314	309
4	253	233
5	166	161
6	159	155
7	145	-141
8	165	151
9	112	-106
H,9,1		
1	225	-213
2	403	371
3	35*	38
4	509	303
5	196	188
6	48	17
7	135	155
8	154	-167
9	31*	31
H,10,1		
0	75	71
1	206	201
2	51	73
3	290	279
4	140	136
5	173	176
6	131	-105
7	61	-69
8	35*	30
H,11,1		
1	276	272
2	164	156
3	75	86
4	195	196
5	253	-256
6	64	47
7	150	-155
8	79	-77
H,12,1		
0	332	322
1	72	61
2	107	103
3	50	50
4	131	-110
5	56	69
6	271	-272
7	31*	-14
H,13,1		
1	62	93
2	65	-82
3	51	58
4	121	-124
5	161	-150
6	31*	5
H,14,1		
0	43*	25
1	89	-107
2	59	58
3	295	-285
4	36*	34
5	98	-80
H,15,1		
1	36*	-9
2	168	-171
3	64	59
4	150	-166
H,16,1		
0	145	-142
1	27*	26
2	35*	-42
H,0,2		
0	1066	-1115
2	233	-248
4	240	226
6	279	267
8	97	82
10	42	-33
H,1,2		
1	368	-424
2	186	183
3	63	-68
4	207	206
5	233	240
6	18*	15
7	169	149
8	97	-84
9	50	46
10	89	-62
H,2,2		
0	148	-148
1	237	238
2	110	87
3	466	474
4	62	50
5	178	175
6	89	83
7	77	-72
8	15*	11
9	178	-184
10	41	66
H,3,2		
1	199	193
2	551	584
3	203	178
4	329	339
5	84	-79
6	18*	8
7	114	-112
8	182	-164
9	69	80
H,4,2		
0	271	276
1	21*	19
2	254	265
3	263	277
4	127	-116
5	118	111
6	186	-202
7	15*	-27
8	114	-113
9	84	-94
H,5,2		
1	310	326
2	29*	-14
3	13*	-0
4	127	-115
5	275	-274
6	16*	3
7	313	-303
8	67	83
9	21*	-31
H,6,2		
0	258	270
1	148	-136
2	186	186
3	229	-233
4	186	-181
5	203	-204
6	296	-293
7	152	145
8	128	-127
9	89	99
H,7,2		
1	42	32
2	258	-266
3	76	71
4	245	-258
5	17*	-36
6	50	-40
7	84	-76
8	97	99
H,8,2		
0	165	-159
1	164	-149
2	76	-67
3	233	-223
4	139	136
5	258	-245
6	161	181
7	93	85
8	63	65
H,9,2		
1	250	-259
2	97	-98
3	59	48
4	195	-208
5	245	238
6	15*	-10
7	139	144
8	50	78
H,10,2		
0	271	-284
1	18*	19
2	139	-136
3	89	94
4	110	90
5	15*	-37
6	120	109
7	10*	8
H,11,2		
1	169	-170
2	254	247
3	67	-84
4	161	155
5	72	68
6	11*	-0
H,12,2		
0	57	-57
1	152	152
2	72	-79
3	250	258
4	13*	27
5	42	40
H,13,2		
1	110	101
2	145	137
3	12*	23
4	84	72
5	50	-65
H,14,2		
0	264	279
1	10*	20
2	93	97
3	42	59
H,0,3		
1	112	-99
3	300	-330
5	149	-148
7	31	58
H,1,3		
1	30	-47
2	189	-177
3	17*	-20
4	209	-192
5	123	117
6	44	-36
7	82	107
H,2,3		
0	289	-300
1	91	90
2	90	-83
3	76	-44
4	134	132
5	52	-50
6	172	196
7	26*	-3
H,3,3		
1	269	-262
2	119	97
3	56	-47
4	90	83
5	195	178
H,4,3		
0	179	-189
1	142	134
2	142	-109
3	172	158
4	27*	-14
5	87	85
H,5,3		
1	45	54
2	300	263
3	60	-56
4	157	153
5	63	-67
H,6,3		
0	165	172
1	112	114
2	142	129
3	202	183
4	90	-90
5	101	96
H,7,3		
1	225	225
2	60	55
3	24*	4
4	33	31
5	87	-66
H,8,3		
0	179	205
1	26*	-42
2	119	119
3	119	-124
4	90	-92
5	63	-67
H,9,3		
1	67	90
2	144	-146
3	33	-24
4	108	-126
H,10,3		
0	37	-32
1	67	-75
2	17*	-31
3	104	-108

Table 4. *Mean atomic and thermal parameters of* $Cu(N_3)_2$ *after anisotropic refinement*

Individual atomic temperature factors were refined for all atoms in the form

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12})\right],$$

with one of the principal axes parallel to [001]. u_r = r.m.s. amplitude of thermal motion along the *r*th principal axis. Positional and thermal parameters are multiplied by 10^4 and standard deviations are given in parentheses. E.s.d.'s of the thermal principal axes are 0·01 Å for the nitrogen atoms and 0·002 Å for Cu.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	u_1	u_2	u_3
N(1)	3305 (13)	1879 (8)	7500	135 (15)	53 (6)	1010 (118)	−51 (8)	0·14 Å	0·22 Å	0·29 Å
N(2)	4099 (9)	2541 (6)	7500	100 (9)	22 (4)	474 (78)	−6 (6)	0·14	0·15	0·21
N(3)	4973 (9)	3208 (6)	7500	68 (9)	30 (4)	600 (82)	−24 (5)	0·12	0·17	0·21
Cu	5803 (1)	3967 (1)	2500	82 (2)	31 (1)	672 (17)	−7 (1)	0·16	0·18	0·19
N(4)	6533 (8)	4782 (5)	7500	49 (7)	19 (4)	661 (76)	−7 (4)	0·12	0·15	0·18
N(5)	7619 (10)	5307 (6)	7500	84 (10)	35 (5)	715 (85)	−25 (6)	0·13	0·19	0·22
N(6)	8561 (18)	5818 (14)	7500	186 (23)	153 (16)	996 (151)	−90 (17)	0·21	0·22	0·42

Table 5. *Some important interatomic distances and angles in* $Cu(N_3)_2$

Standard deviations are given in parentheses.

Superscript	Atom at	
none	$x,\ y,\ z$	with translations
′	$\bar{x},\ \bar{y},\ \frac{1}{2}+z$	with translations
″	$\frac{1}{2}-x,\ \frac{1}{2}+y,\ z$	with translations
‴	$\frac{1}{2}+x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$	with translations

Bonds	$l(\sigma)$	Bonds	$l(\sigma)$
Cu—Cu	3·079 (1) Å	N(1)–N(6′)	3·852 (22) Å
Cu—Cu′	3·497 (2)	N(1)–N(6″)	3·185 (18)
Cu—N(3)	1·995 (5)	N(1)–N(3‴)	3·398 (12)
Cu—N(4)	2·003 (4)	N(1)–N(4‴)	3·155 (10)
Cu—N(1‴)	2·542 (10)	N(1)–N(5‴)	3·378 (11)
Cu—N(4′)	2·709 (7)	N(2)–N(5′)	3·631 (10)
N(1)–N(2)	1·146 (13)	N(2)–N(6′)	3·617 (20)
N(2)–N(3)	1·199 (11)	N(2)–N(6″)	3·145 (18)
N(4)–N(5)	1·213 (11)	N(3)–N(4′)	3·398 (9)
N(5)–N(6)	1·098 (16)	N(3)–N(5′)	3·450 (12)
N(3)–N(4)	2·548 (10)	N(6)–N(6′)	3·750 (23)
		N(3)–N(3)	3·079 (1)

Angles	$\theta(\sigma)$
Cu——N(1‴)–N(2‴)	155·6 (1·0)°
Cu——N(3) —N(2)	129·3 (0·2)
Cu——N(4) —N(5)	126·0 (0·3)
Cu——N(4′)—N(5′)	106·0 (0·6)
N(1‴)–Cu——N(3)	96·3 (0·3)
N(1‴)–Cu——N(4)	87·1 (0·3)
N(3)—Cu——N(3)	101·0 (0·3)
N(3)—Cu——N(4)	79·2 (0·2)
N(3)—Cu——N(4′)	91·2 (0·3)
N(4)—Cu——N(4)	100·5 (0·3)
N(4)—Cu——N(4′)	85·4 (0·2)
N(1)—N(2)—N(3)	177·5 (1·1)
N(4)—N(5)—N(6)	176·8 (1·4)

van der Waals contacts to the environment. This shows up, as mentioned earlier, in a higher thermal motion of N(6), and also as a more pronounced asymmetry of the azido group. The nitrogen–nitrogen distances within both independent N_3 groups are significantly different (see below) and can at least for the most asymmetric group be directly compared with distances found for the organic, covalently bonded azido groups (Gray, 1963). Neither azido group in $Cu(N_3)_2$ departs significantly from linearity:

N(1)	N(2)	N(3)	N(4)	N(5)	N(6)
	177·5 (1·1)°			176·8 (1·4)°	
1·146 (13)	1·199 (11)		1·213 (11)	1·098 (16) Å	
(1·178)	(1·204)		(1·225)	(1·159) Å	

Taking the long Cu–N distances into account the structure can be considered to be built from double chains of linked octahedra sharing edges (Fig. 3). The strings are extended along the *c* axis and form a distorted version of the double chains present in $NH_4[CdCl_3]$(Brasseur & Pauling, 1938).

An interpretation of the anisotropic parameters of Table 4 has at most only a qualitative meaning. This implies that the largest r.m.s. vibration amplitudes are in the directions of smallest constraints and *vice versa*. As shown in Fig. 4, both terminal nitrogen atoms N(1) and N(6) have their largest r.m.s. amplitudes across the N–N–N axes in (001), that is in directions with no N–N or Cu–N bonds and with large packing distances between the nitrogen atoms, 3·2 Å for N(1) and 3·8 Å for N(6). The strong bonds within the azido groups

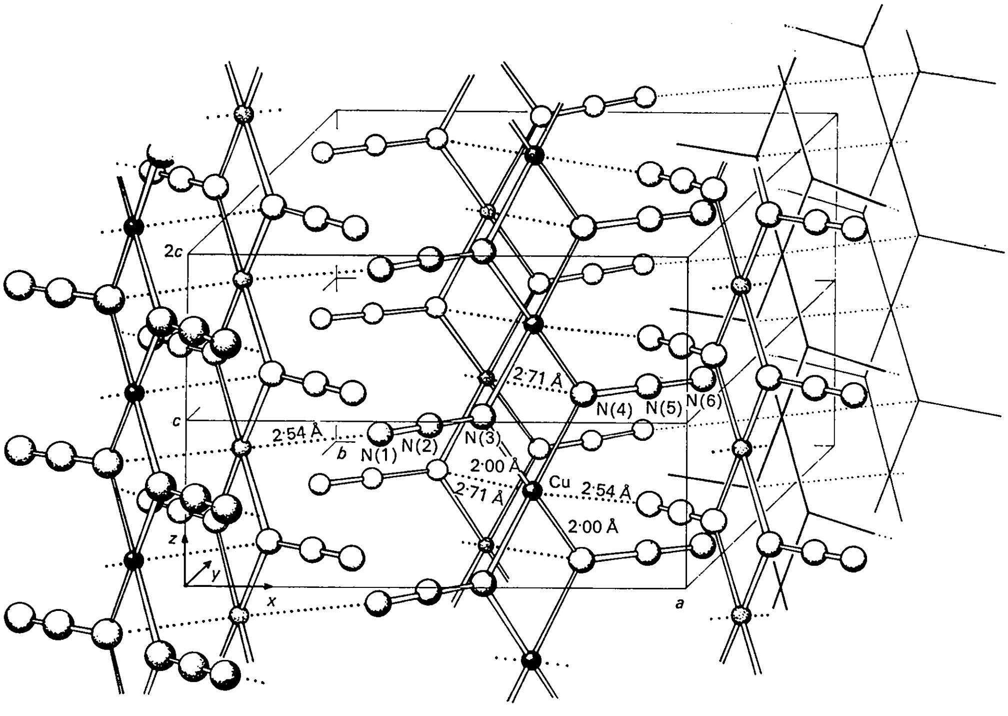

Fig. 3. Perspective view of the crystal structure of $Cu(N_3)_2$.

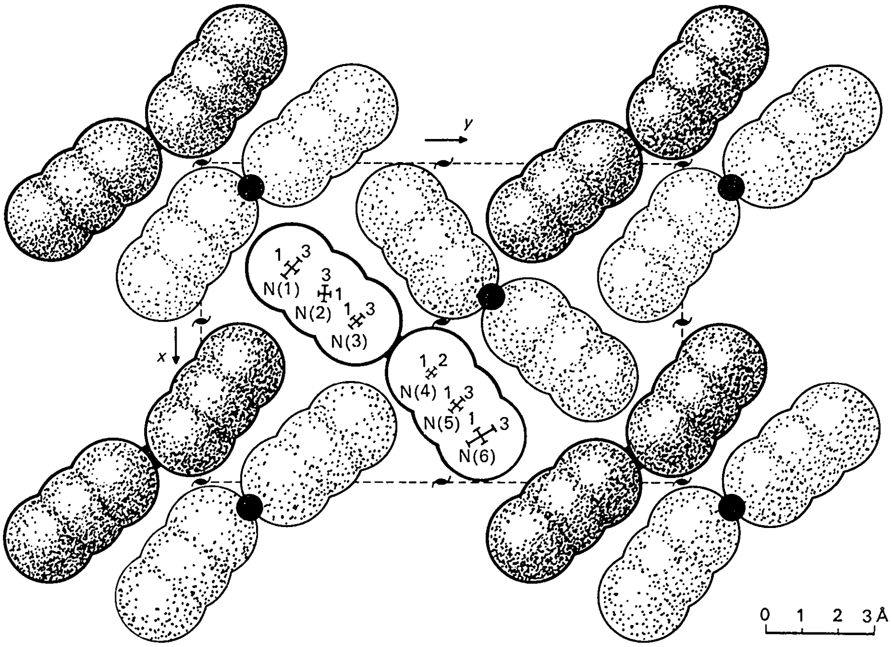

Fig. 4. Packing of the $[Cu(N_3)_2]_n$ chains viewed along [001]. Principle axes of thermal motion, referring to Table 4, are indicated.

and an inspection of the thermal ellipsoids suggest that rigid body angular oscillations (or bending motions) make considerable contributions to the mean square displacements of the nitrogen atoms. Similar results have been obtained from anisotropic refinement of the related structure of *trans*-$[Cu(N_3)_2(NH_3)_2]$ (Söderquist, 1967), using mean values of the observed structure factors of Agrell (1966). Considerable contributions to the r.m.s. amplitudes seem also to arise here from angular oscillations of the azido groups. In this case, however, the largest contributions are normal to the mirror planes containing the N_3 groups, directions in which the constraints of the nitrogen atoms are small.

To get a very rough estimate whether the asymmetry of the azido groups persists when thermal motions are taken into account, corrections were applied to the apparent intra-azido distances assuming the 'riding' motion approximation of Busing & Levy (1964). The results, given within brackets above, indicate that the asymmetry is still significant, although more pronounced for the azido group with the free, non-coordinated end.

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