

The Crystal Structure of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ 

INGELA AGRELL

*Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, P.O.Box, S-402 20 Göteborg 5, Sweden*

The crystal structure of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  has been determined by single crystal X-ray diffraction methods. The crystals are monoclinic and belong to the space group  $P2_1/c$  (No. 14). There are four formula units in the unit cell which has the dimensions  $a=8.528 \pm 0.001$  Å,  $b=20.161 \pm 0.002$  Å,  $c=8.064 \pm 0.001$  Å,  $\beta=106.13 \pm 0.01^\circ$ , and  $V=1331.8$  Å<sup>3</sup>. The zinc atom is tetrahedrally coordinated, the distances to the coordinating nitrogen atoms of the ligands being  $1.93 \pm 0.02$  Å,  $1.95 \pm 0.02$  Å,  $2.01 \pm 0.02$  Å, and  $2.06 \pm 0.02$  Å. The azide groups are almost linear and seem to be asymmetric, the nitrogen-nitrogen distances lying in the range 1.13–1.17 Å, with standard deviations of about 0.03 Å. The  $R$ -value of the proposed structure is 0.075.

The infrared spectrum of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  has also been registered.

During recent years, the author has investigated the crystal structures of some related inorganic azide compounds. The crystal structures of  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$ ,<sup>1</sup>  $\text{Cu}(\text{N}_3)_2$ ,<sup>2,3</sup> and  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>4</sup> have previously been determined, while the crystal structure of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  is presented in this paper. An investigation of the structures of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  and an ammine complex of zinc azide is in progress. Recently, crystal structure determinations of other inorganic azide compounds have been reported in the literature.<sup>23,25</sup>

The compound  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  was first prepared by Dennis and Isham<sup>6</sup> from metallic zinc, an aqueous solution of hydrazoic acid and pyridine,<sup>6</sup> the crystals being described as white. Later, white needle-shaped crystals of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  were prepared by Strecker and Schwinn<sup>7</sup> from  $[\text{Zl.C}_2(\text{C}_5\text{H}_5\text{N})_2]$ , pyridine and  $\text{NaN}_3$ .

## EXPERIMENTAL

*Preparation.* A solution of 1 M  $\text{NaN}_3$  was poured into a solution of 1 M  $\text{Zn}(\text{NO}_3)_2$ , whereupon a precipitate was formed. The mixture was then warmed and the precipitate dissolved by dropping pyridine into the solution. On cooling, colourless needle-shaped crystals of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ , unstable in air, appeared.<sup>8</sup>

*Analysis.* The amount of zinc in  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  was determined by titration with EDTA<sup>9</sup> and the azide content by titration with a Ce(IV)-solution.<sup>10</sup> The following results were obtained: Zn 21.6;  $\text{N}_3^-$  26.9. Calc. for  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ : Zn 21.3;  $\text{N}_3^-$  27.3. The structure determination moreover confirms that  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  is the true formula of the product prepared.

#### STRUCTURE INVESTIGATION

*X-Ray methods.* The single crystals of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  used to record the intensity data were needle-shaped, the needle-axis being parallel to the crystallographic *c*-axis. The crystals rotated about the *b*-axis were cut so that they had a diameter of 0.16 mm, or less, in all directions. Owing to their instability in air, the crystals were mounted in glass capillaries, but seven different crystals had to be used to collect the intensity data. Weissenberg photographs were registered for seventeen zones (*hk0-hk4* and *h0l-h11l*) using  $\text{CuK}\alpha$ -radiation and multiple film equi-inclination techniques. It was noticed that the intensities of the reflexions on the films faded rapidly, when going to higher  $\sin\theta$ -values. Only reflexions with relatively low  $\sin\theta$ -values could therefore be registered.

In order to obtain accurate values for the dimensions of the unit cell, X-ray powder photographs of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  were taken in a Guinier focusing camera, using  $\text{CuK}\alpha_1$ -radiation ( $\lambda = 1.54050 \text{ \AA}$ ) and  $\text{Pb}(\text{NO}_3)_2$  ( $a = 7.8564 \text{ \AA}$ )<sup>11</sup> as an internal standard.

*Unit cell and space group.* The crystals were found to be monoclinic and the approximate cell dimensions obtained from the Weissenberg photographs were refined by means of the Guinier photographs. The  $\sin^2\theta_{\text{obs}}$ -values were obtained from the measured *s*-values using the computer programme PEPP.<sup>12</sup> The cell dimensions were then refined with the programme POWDER,<sup>13</sup> the following values being obtained:  $a = 8.528 \pm 0.001 \text{ \AA}$ ,  $b = 20.161 \pm 0.002 \text{ \AA}$ ,  $c = 8.064 \pm 0.001 \text{ \AA}$ ,  $\beta = 106.13 \pm 0.01^\circ$ , and  $V = 1331.8 \text{ \AA}^3$ . Observed and calculated  $\sin^2\theta$ -values are given, together with observed and calculated intensities, in Table 1.

The density of the crystals, as determined by the flotation method using mixtures of  $\text{CCl}_4$  and  $\text{C}_6\text{H}_6$ , was found to be  $1.5 \text{ g/cm}^3$ . The unit cell thus contains four formula units ( $\rho_{\text{calc}} = 1.53 \text{ g/cm}^3$ ).

It was obvious from the X-ray photographs that the following conditions of reflexion were obeyed: *hkl*: no conditions; *0k0*:  $k = 2n$ ; *h0l*:  $l = 2n$ . This is characteristic for the space group  $P2_1/c$  (No. 14).<sup>11</sup>

*Determination 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 using the programme DATA P2,<sup>13</sup> but no correction was applied for absorption ( $\mu R \leq 0.26$ ).

In space group  $P2_1/c$  there is one fourfold general position and four twofold special positions, the latter positions requiring a centrosymmetrical point symmetry. In order to locate the zinc atom, a three-dimensional Patterson summation, based on the reflexions from *hk0-hk4*, was undertaken using the programme DRF.<sup>13</sup> Approximate scale factors for the different layers were obtained from a comparison of the common reflexions in the *hk0-hk4* layers and the *h2l* layer. Apart from that at the origin, two large peaks were

Table 1. X-Ray powder diffraction data for  $[\text{Zn}(\text{N}_3)_2(\text{C}_6\text{H}_5\text{N})_2]$ . Guinier camera.  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.54050 \text{ \AA}$ ).

$h k l$	$10^6 \times \sin^2\theta_{\text{obs}}$	$10^6 \times \sin^2\theta_{\text{calc}}$	$I_{\text{obs}}$	$I_{\text{calc}}(\text{rel. scale})$
1 1 0	10336	10300	vst	972
0 1 1	11354	11347	w	140
1 2 0	14722	14678	vw	64
-1 1 1	15020	14991	m	232
0 2 1	15720	15725	st	368
-1 2 1	19386	19370	m	152
1 3 0	21960	21976	st	456
1 1 1	25392	25384	m	240
-1 3 1	26664	26667	m	280
1 2 1	29750	29762	w	148
1 4 0	32206	32193	w	116
-1 0 2	37976	37998	vw	42
-1 1 2	39420	39457	w	124
-2 2 1	40644	40695	w	84
0 1 2	40948	41009	vw	33
2 2 0	41221	41200	w	96
-1 2 2	43815	43836	w	116
0 2 2	45388	45388	m	244
0 5 1	46355	46376	w	100
1 4 1	47252	47277	w	68
-2 3 1	48042	47993	m	156
-1 3 2	51086	51134	vw	44
-2 0 2	54089	54127	m	148
-2 1 2	55539	55587	vw	31
2 1 1	57075	57102	w	124
1 0 2	58776	58783	vw	52
-2 2 2	59928	59965	m	152
1 5 1	60395	60413	m	164
2 2 1	61420	61481	w	80
0 6 1	62384	62431	w	116
1 2 2	64569	64622	vw	13
-1 6 1	66073	66075	vw	16
-2 3 2	67205	67263	vw	23
-1 5 2	74527	74487	vw	22
3 0 0	79575	79565	vw	24
1 7 0	80308	80358	vw	24
-2 5 2	90526	90616	vw	31
-2 2 3	98936	99011	vw	24
1 8 0	102225	102252	vw	9
2 6 1	108214	108186	vw	39
-3 5 1	110306	110353	vw	32
-3 4 2	111287	111290	vw	26
2 8 0	128787	128774	vw	36
-2 5 3	129723	129661	vw	22
0 8 2	132963	132962	vw	22
-2 3 4	165166	165129	vw	4
-4 1 3	169544	169541	vw	11
111 0	185426	185446	vw	9

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

observed at (0.00, 0.26, 0.50) and (0.49, 0.50, 0.12) and two other peaks of about half their height at (0.52, 0.24, 0.37) and (0.00, 0.50, 0.50). The two largest peaks could be accounted for if the zinc atom were situated in the fourfold position  $4e$ , with  $x \approx 0.255$ ,  $y \approx 0.120$ , and  $z \approx 0.185$  and this zinc position would also give rise to a peak at (0.00, 0.26, 0.50). If the zinc atom were, however, assumed to be situated in twofold positions only, the vector (0.00, 0.50, 0.50) could be accounted for, but since a twofold position seemed unlikely, owing to symmetry reasons, the peak at (0.00, 0.50, 0.50) was disregarded at this stage. Later it was found that the peak could be explained in terms of vectors between other atoms.

Using the signs of the structure factors obtained when the zinc atom was placed in  $P2_1/c$ :  $4e$  ( $x \approx 0.255$ ,  $y \approx 0.120$ ,  $z \approx 0.185$ ), two electron density projections, one on (001) (cf. Fig. 1) and one on (010) were calculated.<sup>13</sup> It was not possible, from these projections, to locate the positions of the nitrogen and carbon atoms, and a three-dimensional electron density function was therefore calculated, using the reflexions from  $hk0-hk4$ . From the resulting electron density distribution it was possible to locate a tetrahedron of nitrogen atoms surrounding the zinc atom. A new three-dimensional electron density function, based on these assumptions, was calculated and its resolution proved to be sufficient to locate the azide groups. Two successive electron density calcula-

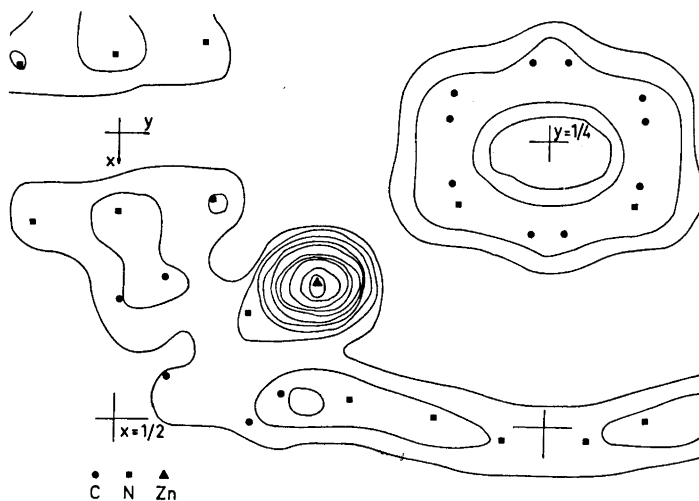


Fig. 1. Electron density projection of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  along the  $c$ -axis. Arbitrary units. The final positions of the atoms are indicated.

tions then revealed the positions of the atoms belonging to the pyridine rings. Thus, the approximate coordinates of all nineteen atoms, all of which are situated in the fourfold position  $4e$ , were obtained.

*Refinement of the structure.* The structural parameters were refined using the least squares programme LALS.<sup>13</sup> In the first stages of the refinement

atomic coordinates and isotropic temperature factors were refined for all atoms, using the reflexion material obtained from rotation about the *c*-axis. The refinement yielded an *R*-value of 0.089 for the *c*-axis data (338 independent reflexions). The reflexion material collected about the *b*-axis was then treated in the same way and gave an *R*-value of 0.071, based on 340 independent reflexions, approximately the same atomic parameters being obtained.

The two sets of data were combined, and a mean value was calculated for those reflexions collected twice, thus giving a total number of 588 independent reflexions. This number was not, however, sufficient for the anisotropic refinement of all atoms. The structure was therefore refined in three different ways. Firstly, the zinc atom and the nitrogen atoms of the azide groups were refined anisotropically, while the other atoms were refined isotropically. Secondly, the zinc atom and the atoms of one of the pyridine rings were refined anisotropically and, thirdly, the zinc atom and the atoms of the other pyridine ring were refined anisotropically. Although the three cases were not found to differ statistically, the lowest standard deviations and *R*-value were obtained when the zinc atom and the atoms of the N(41)–C(45) ring (*cf.* Table 2) were refined anisotropically.

The final cycles of refinement, using the full matrix programme, were thus undertaken with the combined reflexion material, consisting of 588 independent observed reflexions, with anisotropic refinement of the zinc atom and the atoms of the N(41)–C(45) pyridine ring and isotropic refinement of the remaining atoms. Cruickshank's weighting scheme ( $w^{-1} = a + F_o + cF_o^2$ ) was employed with the constants  $a = 12.0$  and  $c = 0.04$ . The relativistic Hartree-Fock X-ray scattering factors<sup>14</sup> were used, and the number of parameters refined was 112. The *R*-value converged to 0.075 and a difference electron density map at this stage showed no spurious peaks. The resulting atomic parameters are given in Table 2, and observed and calculated structure factors are listed in Table 3.

#### IR-SPECTRUM OF $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$

The IR-spectrum of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ , registered on a Beckman IR 9 spectrophotometer, using the KBr technique, is shown in Fig. 2. Most of the bands originate from pyridine, but there are also bands at frequencies at which an asymmetric azide group is expected to absorb. An asymmetric azide group normally shows a very strong band due to stretching ( $\nu_3$ ) just above  $2000\text{ cm}^{-1}$ <sup>15,16</sup> and two weaker bands, one also due to stretching ( $\nu_1$ ) a little above  $1300\text{ cm}^{-1}$  and another due to bending ( $\nu_2$ ) just above  $600\text{ cm}^{-1}$ .<sup>26</sup> In the IR-spectrum of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ , the strong antisymmetric stretching band is split into peaks at  $2070\text{ cm}^{-1}$  and  $2100\text{ cm}^{-1}$ . A similar splitting was found for  $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]$ ,<sup>1</sup> where the two peaks were registered at  $2040\text{ cm}^{-1}$  and  $2080\text{ cm}^{-1}$ , and for  $\text{Cu}(\text{N}_3)_2$ ,<sup>3</sup> where they were registered at  $2080\text{ cm}^{-1}$  and  $2130\text{ cm}^{-1}$ . This splitting suggests the presence of two different azide groups. The two weaker absorption bands are more difficult to locate because they are in the region where pyridine also shows absorption. In order to be able to discard those bands due to pyridine, the IR-spectrum of  $[\text{Zn}(\text{N}_3)_2\text{py}_2]$  was compared with those of  $[\text{ZnCl}_2\text{py}_2]$ ,  $[\text{ZnI}_2\text{py}_2]$ , and  $[\text{Zn}(\text{NCS})_2\text{py}_2]$ .<sup>27</sup> It

Table 2. Atomic coordinates (expressed as fractions of the cell edges) and thermal parameters for  $[\text{Zn}(\text{N}_3)_2(\text{C}_2\text{H}_4\text{N}_2)]_2$ . Anisotropic temperature factors are of the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{13} + 2kl\beta_{23} + 2lh\beta_{31})]$ , and isotropic temperature factors of the form  $\exp[-B(\sin^2\theta/\lambda^2)]$ . The standard deviations are given in parentheses. Space group  $F2_2/c$ .

	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{13}$	$\beta_{23}$	$\beta_{31}$	$B (\text{\AA}^2)$
Zn	0.2582(3)	0.1204(1)	0.1872(3)	0.0305	0.0039	0.0267	-0.0000	0.0106	0.0009	7.710
N(11)	0.4595(19)	0.1408(8)	0.3591(22)							6.576
N(12)	0.4913(19)	0.1866(8)	0.4514(22)							7.769
N(13)	0.5255(19)	0.2265(8)	0.5537(22)							8.366
N(31)	0.1097(19)	0.0562(9)	0.2421(23)							7.010
N(32)	0.1334(18)	0.0015(10)	0.2837(20)							7.831
N(33)	0.1518(19)	-0.0516(9)	0.3305(21)							5.476
N(21)	0.1175(17)	0.1994(6)	0.0955(17)							6.044
C(21)	0.1677(19)	0.2622(9)	0.1317(21)							7.230
C(22)	0.0741(24)	0.3157(10)	0.0720(26)							7.272
C(23)	-0.0794(24)	0.3073(10)	-0.0417(28)							7.013
C(24)	-0.1337(22)	0.2430(9)	-0.0890(22)							7.311
C(25)	-0.0346(25)	0.1924(9)	-0.0149(27)							
N(41)	0.3323(19)	0.0835(7)	-0.0164(18)	0.0257	0.0030	0.0195	0.0063	-0.0009	0.0028	
C(41)	0.4585(25)	0.1106(10)	-0.0602(27)	0.0242	0.0046	0.0252	-0.0001	0.0220	0.0055	
C(42)	0.5002(25)	0.0835(15)	-0.2082(37)	0.0245	0.0082	0.0321	0.0117	0.0281	0.0199	
C(43)	0.4181(34)	0.0303(14)	-0.2371(33)	0.0327	0.0048	0.0357	0.0070	-0.0249	-0.0013	
C(44)	0.2856(39)	0.0042(12)	-0.2414(37)	0.0502	0.0038	0.0329	0.0056	-0.0075	-0.0007	
C(45)	0.2515(25)	0.0315(11)	-0.1032(29)	0.0342	0.0041	0.0223	-0.0003	0.0067	-0.0043	



Table 3. Continued.

-4	H 12 2	-3	-	-2	-2	38	-35	-1	21	23	-7	H 12 4	-3	24	23
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-2	27	27	-1	-	0	40	32	1	5	7	-5	-	-1	30	-28
-1	27	-24	0	28	26	1	-	2	14	13	-6	-	1	-	10
0	-1	27	1	17	17	2	18	-21	3	13	-5	11	11	0	20
0	21	23	3	13	-12				4	25	-22	-4	-	2	26
1	15	17	4	-	-10				5	-	-3	21	-18		-25
2	25	-29				-3	H 14 3		6	7	6	-2	7	H 2 5	
3	-	-5				-2	-					-1	24	-5	14
4	15	14				-1	35					0	7	-4	25
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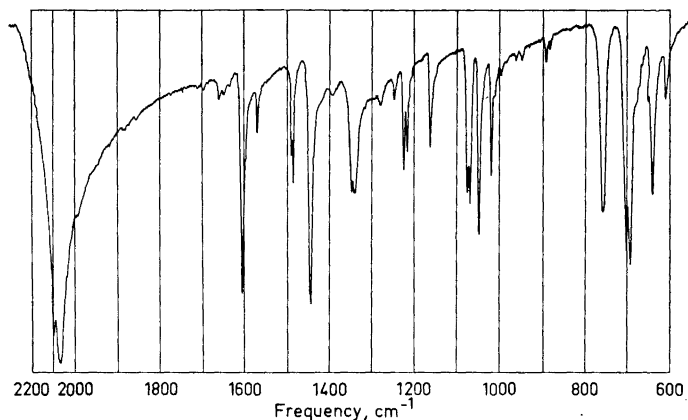


Fig. 2. Infrared spectrum of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  (The monochromator was changed at  $2000\text{ cm}^{-1}$ ).

then seemed likely that the split band with peaks at  $1340\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$  ought to arise from the symmetric stretching and that at  $610\text{ cm}^{-1}$  from the bending of the azide group.

#### DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of one formula unit of the compound  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ , projected along the  $a$ -axis is reproduced in Fig. 3. Fig. 4 is a projection along

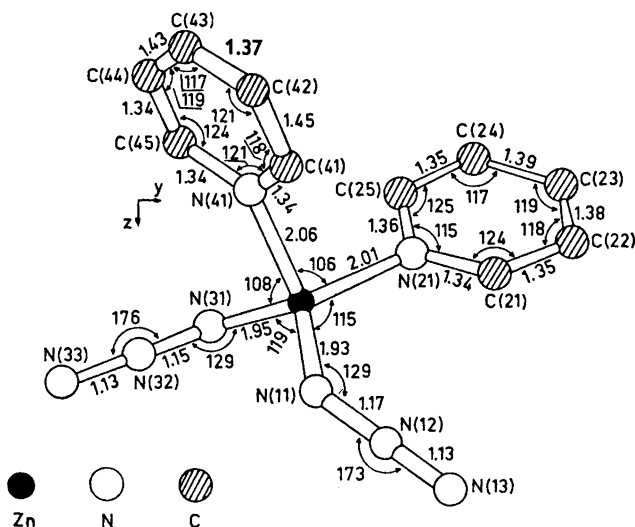


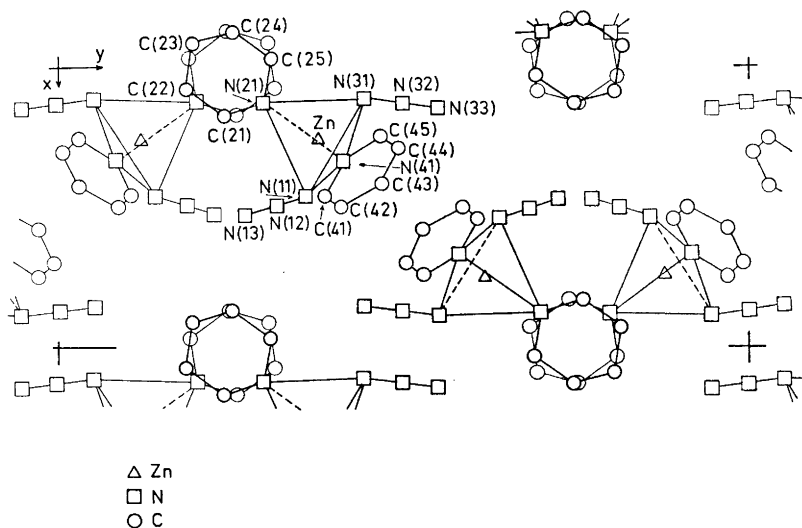
Fig. 3. A molecule of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  projected along the  $a$ -axis. Distances in Å and angles in degrees.

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

a) Zn—N distances within the coordination sphere:		Distance (Å)
N(11)[0.46, 0.14, 0.36]—Zn[0.26, 0.12, 0.19]		1.928(16)
N(21)[0.12, 0.20, 0.10]—Zn[0.26, 0.12, 0.19]		2.008(13)
N(31)[0.11, 0.06, 0.24]—Zn[0.26, 0.12, 0.19]		1.945(17)
N(41)[0.33, 0.08, -0.02]—Zn[0.26, 0.12, 0.19]		2.055(15)
b) N—N distances within the azide groups:		
N(12)[0.49, 0.19, 0.45]—N(11)[0.46, 0.14, 0.36]		1.170(23)
N(13)[0.53, 0.23, 0.55]—N(12)[0.49, 0.19, 0.45]		1.131(24)
N(13)[0.53, 0.23, 0.55]—N(11)[0.46, 0.14, 0.36]		2.297(23)
N(32)[0.13, 0.00, 0.28]—N(31)[0.11, 0.06, 0.24]		1.153(27)
N(33)[0.15, -0.05, 0.33]—N(32)[0.13, 0.00, 0.28]		1.133(26)
N(33)[0.15, -0.05, 0.33]—N(31)[0.11, 0.06, 0.24]		2.284(25)
c) N—C and C—C distances within the pyridine rings:		
C(21)[0.17, 0.26, 0.13]—N(21)[0.12, 0.20, 0.10]		1.343(21)
C(25)[-0.03, 0.19, -0.01]—N(21)[0.12, 0.20, 0.10]		1.361(25)
C(22)[0.07, 0.32, 0.07]—C(21)[0.17, 0.26, 0.13]		1.350(26)
C(23)[-0.08, 0.31, -0.04]—C(22)[0.07, 0.32, 0.07]		1.384(28)
C(24)[0.87, 0.24, 0.91]—C(23)[0.92, 0.31, 0.96]		1.394(27)
C(25)[0.97, 0.19, 0.99]—C(24)[0.87, 0.24, 0.91]		1.353(27)
C(41)[0.46, 0.11, 0.94]—N(41)[0.33, 0.08, 0.98]		1.339(25)
C(45)[0.25, 0.03, 0.90]—N(41)[0.33, 0.08, 0.98]		1.341(27)
C(42)[0.50, 0.08, 0.79]—C(41)[0.46, 0.11, 0.94]		1.445(35)
C(43)[0.42, 0.03, 0.70]—C(42)[0.50, 0.08, 0.79]		1.370(39)
C(44)[0.29, 0.00, 0.76]—C(43)[0.42, 0.03, 0.70]		1.426(41)
C(45)[0.25, 0.03, 0.90]—C(44)[0.29, 0.00, 0.76]		1.344(36)
d) Selected distances other than bond distances:		
N(11)[0.46, 0.14, 0.36]···N(41)[0.33, 0.08, 0.98]		3.139(22)
N(31)[0.11, 0.06, 0.24]···N(41)[0.33, 0.08, 0.98]		3.232(22)
N(21)[0.12, 0.20, 0.10]···N(41)[0.33, 0.08, 0.98]		3.247(20)
N(31)[0.11, 0.06, 0.24]···N(11)[0.46, 0.14, 0.36]		3.337(23)
N(21)[0.12, 0.20, 0.10]···N(11)[0.46, 0.14, 0.36]		3.313(21)
N(21)[0.12, 0.20, 0.10]···N(31)[0.11, 0.06, 0.24]		3.127(22)
C(21)[0.17, 0.24, 0.63]···N(13)[0.53, 0.23, 0.55]		3.290(22)
C(41)[0.46, 0.39, 0.44]···N(13)[0.53, 0.23, 0.55]		3.415(26)
C(42)[0.50, 0.92, 0.21]···N(33)[0.15, 0.95, 0.33]		3.437(27)
C(45)[-0.25, 0.97, 0.10]···N(33)[0.15, 0.95, 0.33]		3.442(26)
C(23)[0.08, 0.81, 0.54]···N(33)[0.15, 0.95, 0.33]		3.458(26)

Table 5. Angles in  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ . Notation as in Table 4.

a) N—Zn—N angles within the coordination sphere:				Angle (°)
N(11)[0.46, 0.14, 0.36]	—Zn[0.26, 0.12, 0.19]	—N(21)[0.12, 0.20, 0.10]		114.7(0.6)
N(11)[0.46, 0.14, 0.36]	—Zn[0.26, 0.12, 0.19]	—N(31)[0.11, 0.06, 0.24]		119.0(0.7)
N(11)[0.46, 0.14, 0.36]	—Zn[0.26, 0.12, 0.19]	—N(41)[0.33, 0.08, -0.02]		104.0(0.7)
N(21)[0.12, 0.20, 0.10]	—Zn[0.26, 0.12, 0.19]	—N(31)[0.11, 0.06, 0.24]		104.5(0.6)
N(21)[0.12, 0.20, 0.10]	—Zn[0.26, 0.12, 0.19]	—N(41)[0.33, 0.08, -0.02]		106.1(0.6)
N(31)[0.11, 0.06, 0.24]	—Zn[0.26, 0.12, 0.19]	—N(41)[0.33, 0.08, -0.02]		107.8(0.7)
b) Zn—N—N and N—N—N angles for the azide groups:				
Zn [0.26, 0.12, 0.19]	—N(11)[0.46, 0.14, 0.36]	—N(12)[0.49, 0.19, 0.45]		128.9(1.3)
Zn [0.26, 0.12, 0.19]	—N(31)[0.11, 0.06, 0.24]	—N(32)[0.13, 0.00, 0.28]		129.0(1.3)
N(11)[0.46, 0.14, 0.36]	—N(12)[0.49, 0.19, 0.45]	—N(13)[0.53, 0.23, 0.55]		173.2(2.0)
N(31)[0.11, 0.06, 0.24]	—N(32)[0.13, 0.00, 0.28]	—N(33)[0.15, -0.05, 0.33]		176.3(1.9)
c) Angles within the pyridine rings:				
C(41)[0.46, 0.11, 0.94]	—N(41)[0.33, 0.08, 0.98]	—C(45)[0.25, 0.03, 0.90]		121.1(1.7)
N(41)[0.33, 0.08, 0.98]	—C(41)[0.46, 0.11, 0.94]	—C(42)[0.50, 0.08, 0.79]		117.6(1.8)
C(41)[0.46, 0.11, 0.94]	—C(42)[0.50, 0.08, 0.79]	—C(43)[0.42, 0.03, 0.70]		121.4(2.2)
C(42)[0.50, 0.08, 0.79]	—C(43)[0.42, 0.03, 0.70]	—C(44)[0.29, 0.00, 0.76]		117.3(2.4)
C(43)[0.42, 0.03, 0.70]	—C(44)[0.29, 0.00, 0.76]	—C(45)[0.25, 0.03, 0.90]		118.9(2.4)
N(41)[0.33, 0.08, 0.98]	—C(45)[0.25, 0.03, 0.90]	—C(44)[0.29, 0.00, 0.76]		123.6(2.1)
C(21)[0.17, 0.26, 0.13]	—N(21)[0.12, 0.20, 0.10]	—C(25)[ -0.04, 0.19, -0.02]		115.3(1.4)
N(21)[0.12, 0.20, 0.10]	—C(21)[0.17, 0.26, 0.13]	—C(22)[0.07, 0.32, 0.07]		123.8(1.6)
C(21)[0.17, 0.26, 0.13]	—C(22)[0.07, 0.32, 0.07]	—C(23)[ -0.08, 0.31, -0.04]		119.6(1.8)
C(22)[1.07, 0.32, 1.07]	—C(23)[0.92, 0.31, 0.96]	—C(24)[0.87, 0.24, 0.91]		118.5(1.8)
C(23)[0.92, 0.31, 0.96]	—C(24)[0.87, 0.24, 0.91]	—C(25)[0.97, 0.19, 0.99]		117.4(1.7)
N(21)[1.12, 0.20, 1.10]	—C(25)[0.97, 0.19, 0.99]	—C(24)[0.87, 0.24, 0.91]		125.2(1.7)

Fig. 4. A projection of a unit cell along the  $c$ -axis illustrating the packing of the  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  molecules.

the *c*-axis which illustrates the packing of the molecules of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ . Atomic distances and angles have been calculated by the programme DISTAN<sup>13</sup> and are given in Tables 4 and 5. A comparison of the corresponding distances and angles found in the related structures  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>4</sup> and  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  is given in Table 6.

The zinc atom is surrounded by four nitrogen atoms (Fig. 3), two of which are end atoms of an azide group, the other two originating from pyridine rings. The distances from the central zinc atom to the nitrogen atoms of the two azide groups are  $1.93 \pm 0.02 \text{ \AA}$  and  $1.95 \pm 0.02 \text{ \AA}$  and to the nitrogen atoms of the pyridine rings  $2.01 \pm 0.02 \text{ \AA}$  and  $2.06 \pm 0.02 \text{ \AA}$ . The Zn–N distances reported in the literature for tetrahedral configuration, are 2.0 and 2.1,<sup>17</sup> and in the compound  $\text{Zn}(\text{C}_5\text{H}_4\text{O}_2\text{N})_2(\text{H}_2\text{O})_4$ ,<sup>28</sup> determined at this Department, in which Zn is octahedrally coordinated, the two Zn–N distances were found to be  $2.10 \pm 0.01 \text{ \AA}$ . It appears as if the distances from the zinc atom in  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  to the nitrogen atoms of the azide groups were shorter than those to the nitrogen atoms of the pyridine rings, the same situation having been indicated in the compound  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  (Table 6). There,

Table 6. Comparison of distances (Å) and angles (°) found in  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>4</sup> and  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ . The standard deviations are given in parentheses.

	$[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$	$[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$
Me–N distances (N part of azide group)	1.98(3), 2.01(2)	1.93(2), 1.95(2)
Me–N distances (N part of pyridine ring)	2.04(1), 2.04(1)	2.01(1), 2.06(2)
Azide groups:		
I N–N distances	1.14(4), 1.08(4)	1.17(2), 1.13(2)
Me–N–N angle	127(3)	129(1)
N–N–N angle	177(4)	173(2)
II N–N distances	1.23(3), 1.19(4)	1.15(3), 1.13(3)
Me–N–N angle	119(2)	129(1)
N–N–N angle	178(3)	176(2)
Pyridine rings:		
I N–C distances	1.34(4), 1.32(4)	1.34(2), 1.36(3)
C–C distances	1.42(4), 1.28(4)	1.35(3), 1.38(3)
	1.43(4), 1.37(4)	1.39(3), 1.35(3)
C–N–C angle	120(2)	115(1)
C–C–N angles	119(2), 125(2)	124(2), 125(2)
C–C–C angles	114(2), 123(2), 119(2)	120(2), 119(2), 117(2)
II N–C distances	see above	1.34(3), 1.34(3)
C–C distances		1.45(4), 1.37(4)
		1.43(4), 1.34(4)
C–N–C angle		121(2)
C–C–N angles		118(2), 124(2)
C–C–C angles		121(2), 117(2), 119(2)

the values found were  $1.98 \pm 0.03 \text{ \AA}$  and  $2.01 \pm 0.02 \text{ \AA}$  for the copper-nitrogen distances to the azide groups and  $2.04 \pm 0.01 \text{ \AA}$  for the copper-nitrogen distances to the pyridine rings. The four nitrogen atoms form an almost regular tetrahedron about the central zinc atom, the lengths of the edges of the tetrahedron lying between  $3.13 \pm 0.02 \text{ \AA}$  and  $3.34 \pm 0.02 \text{ \AA}$  (Table 4). The longest distance is that between the two corners of the tetrahedron at which the azide groups are bonded. A tetrahedral configuration of ligands about zinc is very common.<sup>18</sup>

The two azide groups are crystallographically different, and although no statistical evidence can be provided, they appear to be asymmetric, as in the related structures.<sup>1-4</sup> The asymmetry is, moreover, supported by the appearance of the symmetric stretching ( $\nu_1$ ) band at  $1340 \text{ cm}^{-1}$  and  $1350 \text{ cm}^{-1}$  in the IR-spectrum. The nitrogen-nitrogen distances are N(11)–N(12)  $1.17 \pm 0.02 \text{ \AA}$ , N(12)–N(13)  $1.13 \pm 0.02 \text{ \AA}$  and N(31)–N(32)  $1.15 \pm 0.03 \text{ \AA}$ , N(32)–N(33)  $1.13 \pm 0.03 \text{ \AA}$ , the longer N–N distance being, as expected,<sup>21</sup> closer to the metal-nitrogen bond. The azide groups are almost linear, the N(11)–N(12)–N(13) angle being  $173.2 \pm 2.0^\circ$  and the N(31)–N(32)–N(33) angle  $176.3 \pm 1.9^\circ$ . These distances and angles are in agreement with those found in other inorganic azide compounds<sup>1-4,22,23</sup> (Table 6).

The two pyridine rings are also crystallographically independent, and the distances and angles within the rings (Fig. 3, Tables 4 and 5) are in agreement with those found in  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  (Table 6) and those reported for pure pyridine.<sup>19,20</sup> The best planes through the atoms of the pyridine rings in  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  were obtained by least squares calculation, using the programme PLANEFIT<sup>13</sup> (Table 7). The rings were found to be planar within the limits of error, and the zinc atom is situated approximately in the plane of each pyridine ring, the distance from the zinc atom to the plane of the N(21)–C(25) ring being  $0.04 \text{ \AA}$  and to the plane of the N(41)–C(45) ring  $0.05 \text{ \AA}$ . The angle between the planes through the two different pyridine rings in one formula unit is  $80^\circ$ .

Table 7. Best least squares planes through the pyridine rings (Cartesian coordinates in  $\text{\AA}$ ) and deviations from these planes.

1. Plane through N(21)–C(25):

$$0.6337 X + 0.0225 Y - 0.7733 Z = 0.0257$$

Atom	Deviation( $\text{\AA}$ )	Atom	Deviation( $\text{\AA}$ )
N(21)	–0.008	C(23)	–0.006
C(21)	0.024	C(24)	0.022
C(22)	–0.016	C(25)	–0.015
		Zn	0.037

2. Plane through N(41)–C(45):

$$-0.4835 X + 0.6309 Y - 0.6068 Z = -0.2569$$

Atom	Deviation( $\text{\AA}$ )	Atom	Deviation( $\text{\AA}$ )
N(41)	0.008	C(43)	–0.008
C(41)	–0.009	C(44)	0.006
C(42)	0.009	C(45)	–0.007
		Zn	0.046

The bonds between the central zinc atom and its ligands are probably almost entirely of  $\sigma$ -type, but the possibility of  $\pi$ -back bonding cannot perhaps be entirely excluded.<sup>21-24</sup> The bonds between different units of  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  are of van der Waals order, the shortest C...N distances being approximately 3.4 Å (Table 4), where C is a member of a pyridine ring and N is the end atom of an azide group. The units are packed in such a way that the pyridine rings N(21)–C(25) are almost parallel to each other and form a column in the direction of the *c*-axis (Fig. 4). The distance between two consecutive rings is 3.7 Å, and the angle between their planes is 2.6°. The N(41)–C(45) pyridine rings are packed in pairs, and are parallel to one another owing to symmetry reasons, the distance between them being 3.6 Å.

All computer calculations were performed on an IBM 360/50 computer at the Gothenburg Universities' Computing Centre.

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