The Crystal Structure of Diazidodiamminezinc(II),

[Zn(N₃)₂(NH₃)₂]

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The crystal structure of diazidodiamminezinc(II), [Zn(N₃)₂(NH₃)₂], has been determined by single crystal X-ray diffraction methods.

The crystals belong to the space group *Pnma* (No. 62). The elementary cell contains eight formula units and has the dimensions $a = 9.565 \pm 0.002$ Å, $b = 7.158 \pm 0.002$ Å, $c = 18.976 \pm 0.003$ Å, and $V = 1299.2$ Å³. The coordination around zinc is tetrahedral, the distances from the central zinc atom to the coordinating nitrogen atoms of the ligands lying between 2.03 Å and 1.97 Å, with standard deviations of about 0.02 Å. The azide groups are almost linear and appear to be asymmetric, the nitrogen—nitrogen distances lying in the range 1.14 Å — 1.20 Å, with standard deviations about 0.03 Å.

The infrared spectrum of [Zn(N₃)₂(NH₃)₂] has also been registered.

An investigation of the crystal and molecular structures of a group of related inorganic metal azides is being performed at this Department. In this series, the crystal structures of [Cu(N₃)₂(NH₃)₂],[1] Cu(N₃)₂,[2,3] [Cu(N₃)₂(C₅H₅N)₂],[4] [Zn(N₃)₂(C₅H₅N)₂],[5] and [Cd(N₃)₂(C₅H₅N)₂][6] have previously been determined. Some very preliminary results concerning the structure of [Zn(N₃)₂(NH₃)₂] have been reported earlier,[7] and the complete crystal structure determination is now presented in this paper.

The compound [Zn(N₃)₂(NH₃)₂] was first reported by Dennis and Isham.[8] They obtained diazidodiamminezinc(II) by passing dry gaseous ammonia through an alcoholic solution of zinc azide, the product being subsequently freed from ammonium azide by fractional crystallization. The crystals were described as large, white needles. Later, Strecker and Schwinn [9] attempted to prepare the compound from solutions of zinc azide and ammonia, but their attempts were unsuccessful.

EXPERIMENTAL

Preparation. The preparation of [Zn(N₃)₂(NH₃)₂] was attempted by several methods, and it appeared to be impossible to obtain the compound from aqueous solutions of the reagents. The method eventually employed was based on solubility differences in liquid

Fig. 1. The apparatus used in the preparation of $[Zn(N_3)_2(NH_3)_2]$. KN_3 was placed in A, and $Zn(NO_3)_2$ in B. The gaseous ammonia was led in at C, and was condensed, by cooling, in B, after which KN_3 was allowed to fall down into B. During filtration, the nob at D was replaced by equipment E.
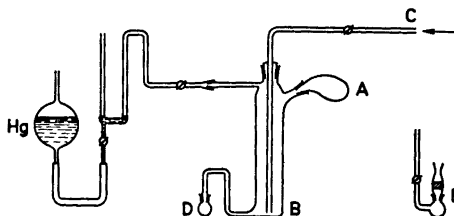
ammonia, and the apparatus used is illustrated in Fig. 1. Thus, when 1.0 g potassium azide and 2.3 g zinc nitrate were dissolved in liquid ammonia at about $-40°C$, a precipitate was formed, which was assumed to be potassium nitrate because of its relatively low solubility in liquid ammonia.[10-12] The mixture was then filtered at $-40°C$, after which the temperature of the filtrate was slowly raised to about $+20°C$. The ammonia gas was allowed to evaporate, and the filtrate solidified. After standing in gaseous ammonia at atmospheric pressure, for, on occasion, a period of up to several months, a colourless liquid appeared over the solid phase. This liquid was poured off and allowed to stand in dry air, whereupon colourless crystal needles of $[Zn(N_3)_2(NH_3)_2]$ were deposited. The crystals tended to be very unstable and disintegrated rapidly, especially on exposure to X-ray radiation.

Analysis. It was not possible to perform an accurate quantitative analysis of the crystals used for the X-ray investigation, as the mother liquor solidified together with the crystals. The chemical analysis performed at this Department, as well as by a commercial laboratory,[13] yielded ambiguous results. At this Department, the zinc amount was determined by titration with EDTA,[14] the azide content by titration with a Ce(IV) solution,[15] and the ammine content by means of a Kjeldahl apparatus.[16] It was thus established[13,17] that the product analysed contained zinc and nitrogen as azide and as ammonia. There appeared, moreover, to be oxygen present,[13] owing to qualitative tests,[18] probably as nitrate.[17] According to the results of the crystal structure determination, the nitrate must, however, originate from adhering mother liquor. The results of one of the quantitative analyses may be mentioned as an example. In this case, all determinations were performed on the same sample. The experimental values obtained were:[13] Zn 33.0 %, N (total) 47.9 %, N (as NH_3) 14.0 %, O 15.8 %, and H 4.0 %. If all oxygen is assumed to originate from a zinc nitrate compound, it can be deduced that this particular sample contains 63.1 % by weight of $[Zn(N_3)_2(NH_3)_2]$ and 32.9 % of a compound of the formula $Zn(NO_3)_2.2NH_3$. The calculated values would then be: Zn 33.3 %, N (total) 47.8 %, N (as NH_3) 14.3 %, O 15.8 %, and H 3.1 %. Other samples yielded different oxygen contents (ranging from 8 % to 16 %) which indicated varying amounts of adhering solidified mother liquor. The structure determination, according to which the formula of the compound investigated is $[Zn(N_3)_2(NH_3)_2]$, must, therefore, be considered to provide the most valid analysis of the compound.

STRUCTURE INVESTIGATION

X-Ray methods. The single crystals of $[Zn(N_3)_2(NH_3)_2]$ used to collect the intensity data were needle-shaped, the needle axis being parallel to the crystallographic *b*-axis. The dimensions of the crystals used were of the magnitude of $0.10 \times 0.15 \times 0.10$ mm. Because the crystals were very unstable, and disintegrated rapidly in the X-ray radiation, several different crystals, mounted in capillaries, had to be used.

Three sets of Weissenberg photographs were collected. The first set, comprising data from the $h0l - h4l$ layers, was recorded in 1962 with $CuK\alpha$-radiation, using multiple film, non-integrating, equi-inclination Weissenberg

techniques. The set of data obtained, which is denoted by A in the following, was of rather poor quality. A new set of multiple film, integrated, Weissenberg photographs of the $h0l-h3l$ layers (B) were collected in 1969 with $CuK\alpha$-radiation. In 1970, the latter data set was extended by two further layer lines, $h4l$ and $h5l$, collected from new crystals using $CuK\alpha$-radiation and integrating techniques. The enlarged data set is denoted by C.

In order to determine accurate cell dimensions, X-ray powder photographs were taken in a Guinier focusing camera, using $CuK\alpha_1$-radiation ($\lambda = 1.54050$ Å) and KCl ($a = 6.2929$ Å)[19] as an internal standard.

Unit cell and space group. The crystals were found to be orthorhombic, and the approximate cell dimensions obtained from the Weissenberg photographs were refined, using the Guinier photographs. When different Guinier photographs were compared, it was observed that they were not identical. This was probably due to the presence of impurities from the mother liquor. Only those lines which appeared in all photographs were therefore used in the refinement. The $\sin^2\theta_{obs}$-values were obtained from the measured s-values, using the computer programme PEPP.[20] The refinement of the cell dimensions was performed by means of the programme POWDER,[21] the following values being obtained: $a = 9.565 \pm 0.002$ Å, $b = 7.158 \pm 0.002$ Å, $c = 18.976 \pm 0.003$ Å, and $V = 1299.2$ 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 CCl_4 and $CHBr_3$. The density found was 1.9 g/cm^3, which corresponds to eight formula units in the unit cell ($\varrho_{calc} = 1.88$ g/cm^3).

Table 1. X-Ray powder diffraction data for $[Zn(N_3)_2(NH_3)_2]$. Guinier camera. $CuK\alpha_1$-radiation ($\lambda = 1.54050$ Å).

$h\,k\,l$	$10^5 \times \sin^2\theta_{obs}$	$10^5 \times \sin^2\theta_{calc}$	I_{obs}	I_{calc} (rel. scale)
1 0 2	1315	1308	w	19
1 1 1	1968	1971	m	73
0 0 4 } 0 1 3 }	2636	2636 } 2641 }	m	90
1 0 4 } 1 1 3 }	3285	3285 } 3289 }	w	36
2 1 0	3752	3752	vw	17
0 2 0	4627	4631	m	79
2 0 4 } 2 1 3 }	5231	5230 } 5235 }	st	116
2 2 1	7391	7390	vw	18
1 2 4	7913	7916	vw	19
2 2 3	8703	8708	vw	13
0 1 7	9230	9231	vw	13
2 2 4	9864	9862	vw	13
2 1 7	11821	11825	vw	13
2 3 7	21090	21088	vw	4
4 2 7	23078	23080	vw	6

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

From the Weissenberg photographs it was obvious that the following conditions of reflection were obeyed: hkl, no conditions; $0kl$, $k+l=2n$; $h0l$, no conditions; $hk0$, $h=2n$. This is characteristic for the space groups $Pn2_1a$ (No. 33)* and $Pnma$ (No. 62).[22]

Determination of the structure. The intensities of the reflections 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 [21] (the data collected in 1962 were corrected graphically), but no correction was applied for absorption, since μR was less than 0.25 for all crystals used.

The structure investigation was started in 1962 with the data set, A, available at that time. The computer calculations were performed on Alwac III E, using the two-dimensional Fourier programme 05 − 28 [23] and the structure factor programme KGK-1.[24] The approximate x- and z-coordinates of the zinc atoms were obtained, but attempts to locate the ligand atoms proved to be unsuccessful.

A new attempt at a complete structure determination was begun in 1969 with the intensity data B. The space group was assumed to be $Pn2_1a$, since this contains $Pnma$ as a special case. A three-dimensional Patterson summation, based on the reflections from $h0l − h2l$, was undertaken, using the programme DRF.[21] The layers were scaled together, assuming a linear relationship between intensity and time of exposure. This yielded, however, an extremely approximate scaling, owing to the disintegration of the crystal.

The largest peaks, excluding that at the origin, were observed at: (0.50, 0.00, 0.00), (0.50, 0.00, 0.28), (0.00, 0.00, 0.28), (0.08, 0.50, 0.50), (0.50, 0.27, 0.50), (0.50, 0.50, 0.00), and (0.08, 0.50, 0.22) (heights 500 − 200 in arbitrary units). Different zinc positions were compatible with these peaks, and electron density calculations [21] were performed for the most probable cases, using the phases of the structure factors thus obtained. In this way, it was possible to obtain approximate positions of the zinc atoms, which agreed fairly well with the Patterson peaks and were supported by the form of the calculated electron density distribution. Zn(1) was thus assigned the fourfold position $4a$ of space group $Pn2_1a$, with $x\approx 0.21$ and $z\approx 0.25$. As y for the first atom in this space group may be chosen at random, it was assigned the value 0.25, this value being in accordance with the fourfold position $4c$ of space group $Pnma$. Zn(2) was found to have approximately the same y-coordinate as Zn(1), and was assigned the position $Pn2_1a$: $4a$ with $x\approx 0.73$, $y\approx 0.25$, and $z\approx 0.53$. Assuming these positions for the zinc atoms, all the largest peaks, except that at (0.50, 0.27, 0.50), could be approximately accounted for by Zn − Zn vectors. These positions ought, however, to give rise to other peaks due to Zn − Zn vectors in the Patterson map. These could, in fact, be located as smaller peaks (heights 200 − 100 in arbitrary units). The peak at (0.50, 0.27, 0.50) was later shown to originate from overlapping Zn − N vectors.

From the electron density calculation (*cf.* Fig. 2), based on the above preliminary positions of the zinc atoms, it appeared that most of the light atoms were situated in the same planes as the zinc atoms, but that there were also some light atom peaks above and below these planes.

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* Orientation differing from that given in the *International Tables.* [22]
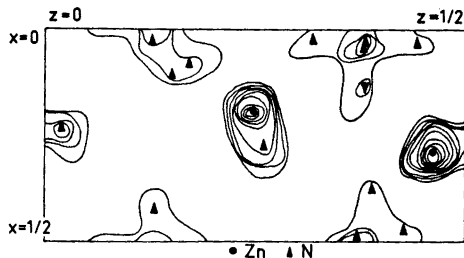
Fig. 2. Electron density projection of [Zn(N$_3$)$_2$(NH$_3$)$_2$] along the b-axis. Arbitrary units. The final positions of the atoms are indicated.

Since the quantitative analysis yielded ambiguous results concerning the composition of the compound, several possibilities with respect to ligand nature and configuration had to be considered. Another difficulty was provided by the fact that reflections from only three layers were at that time available, resulting in rather large termination errors. Electron density maps, together with difference electron density maps, were thus calculated for different suggestions, using the appropriate phases. It became, moreover, apparent that the centrosymmetrical space group *Pnma* might equally well be used, and it was therefore adopted in the subsequent calculations.

A tetrahedral arrangement of four light atoms around each zinc atom was first located. Two of the light atoms occupied a fourfold position, 4c, and were thus situated in the same plane as the zinc atom, the other two being generated from one atom in the eightfold position 8d. As the details of the structure became more clear, by means of the trial and error methods described, and, in the later stages, with the help of data from an additional layer (h3l), it appeared that the data set could be completely explained, assuming all ligand atoms to be nitrogen atoms of either ammonia or azide groups, the compound thus having the formula [Zn(N$_3$)$_2$(NH$_3$)$_2$]. The ammine nitrogen atoms were found to be situated in the position 8d, while the nitrogen atoms of the azide groups all occupied the position 4d. Approximate coordinates for the sixteen crystallographically different atoms were, thus, obtained.

Refinement of the structure. The preliminary atomic positions were obtained on the basis of data set B. The three different sets of data, A, B and C, were used separately in the refinement of the structural parameters by means of the least squares programme LALS.[21] The final atomic positions obtained in the three cases were the same within the limits of error.

In the case of data set A (544 non-integrated, independent reflections from one crystal), all atoms were refined anisotropically, yielding a total of 103 parameters. The R-value obtained was 0.107. In the case of data set B (340 integrated, independent reflections from one crystal), it was not possible to perform anisotropic refinement of all atoms. Four different refinements were therefore carried out, in each of which the zinc atoms and one azide group were refined anisotropically, while the others were refined isotropically. Although there was no statistical difference between the results of the four alternatives, the lowest standard deviations and R-values were obtained in the two cases in which the azide groups N(11) − N(13) and N(31) − N(33) (*cf.* Table 2) were refined anisotropically. The final cycles of refinement based on

this set of data were therefore performed with anisotropic temperature factors for the two zinc atoms and the six nitrogen atoms of the N(11)−N(13) and N(31)−N(33) groups, which entailed a total of 75 parameters to be refined. An R-value of 0.076 was obtained, together with the lowest standard deviations. This is, consequently, considered to be the most accurate determination, and the resulting atomic parameters are given in Table 2. Finally, the atomic parameters were also refined with the intensity data of set C (449 integrated, independent reflections from three different crystals). In this case,

Table 2. Atomic coordinates (expressed as fractions of the cell edges) and thermal parameters for $[Zn(N_3)_2(NH_3)_2]$, based on data set B. Anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hl\beta_{13})]$, and isotropic temperature factors of the form $\exp[-B(\sin^2\theta/\lambda^2)]$. Standard deviations in parentheses. Space group *Pnma*.

Atom		x	y	z	β_{11}	β_{22}	β_{33}	β_{13}	B (Å²)
Zn(1)	4c	0.1879 (04)	0.2500	0.2469 (02)	0.016 (00)	0.028 (02)	0.004 (00)	−0.000 (00)	
Zn(2)	4c	0.7130 (03)	0.2500	0.5386 (02)	0.014 (00)	0.025 (02)	0.004 (00)	−0.001 (00)	
N(11)	4c	0.1063 (25)	0.2500	0.1491 (09)	0.018 (04)	0.054 (15)	0.002 (01)	0.004 (02)	
N(12)	4c	0.9959 (31)	0.2500	0.1277 (13)	0.017 (03)	0.008 (13)	0.004 (01)	0.002 (03)	
N(13)	4c	0.8839 (29)	0.2500	0.1052 (11)	0.021 (04)	0.053 (15)	0.004 (01)	0.008 (03)	
N(21)	4c	0.8340 (22)	0.2500	0.6232 (11)					5.70 (54)
N(22)	4c	0.9554 (21)	0.2500	0.6226 (12)					4.99 (56)
N(23)	4c	0.0777 (27)	0.2500	0.6306 (13)					7.16 (60)
N(31)	4c	0.5168 (21)	0.2500	0.5715 (12)	0.011 (03)	0.051 (12)	0.004 (01)	−0.001 (03)	
N(32)	4c	0.4792 (21)	0.2500	0.6327 (14)	0.008 (02)	0.032 (14)	0.004 (01)	0.002 (02)	
N(33)	4c	0.4331 (25)	0.2500	0.6865 (13)	0.017 (03)	0.059 (13)	0.004 (01)	−0.007 (03)	
N(41)	4c	0.0287 (18)	0.2500	0.3153 (11)					4.74 (50)
N(42)	4c	0.0289 (21)	0.2500	0.3772 (13)					5.12 (59)
N(43)	4c	0.0231 (26)	0.2500	0.4375 (14)					7.47 (70)
N(1)	8d	0.2938 (13)	0.4942 (27)	0.2566 (06)					5.14 (32)
N(2)	8d	0.7404 (12)	0.4821 (24)	0.4819 (06)					5.08 (31)

all atoms, except the nitrogen atoms of the ammine groups, were refined anisotropically, this giving a total of 93 parameters. This yielded an R-value of 0.085, and somewhat higher standard deviations than those obtained in the previous refinement. Since the data set C is that which contains data from the largest number of layer lines, the observed structure factors listed, together with the calculated structure factors, in Table 3 originate from this set.

In all refinements, which were carried out with the full matrix programme, Cruickshank's weighting scheme ($w^{-1}=a+F_o+cF_o^2$) was employed, with the constants $a=5.0$ and $c=0.03$. The relativistic Hartree-Fock X-ray scattering factors [31] were used, the real part of the atomic scattering factor of the zinc atoms being corrected for anomalous dispersion.[32] Difference electron density maps were calculated for all three data sets, and none of them showed any peaks higher than 1.2 electrons/Å³. Distances and angles were calculated by the programme DISTAN [21] and are given in Tables 4 and 5.

Table 3. Observed and calculated structure factors for [Zn(N₃)₂(NH₃)₂], based on data set C. The columns are, l, $|F_{obs}|$ and F_{calc}, respectively. Unobserved reflections are denoted by a dash.

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  0  0  L        15   -    2      12   -   -2      18   16   17               1  2  L          6  2  L
 4  84   61      16   -    4      13   7   -8      19   -   -7           1   14  -14       0  49  -46
 6  72  -74      17  21   20                                             2   57  -56       1  45   48
 8 142  126      18   -   -9       10  0  L           4  1  L            3    -   -8        2  15   13
10 116 -112      19   -    3       0  17   18      0  112   98           4  121 -107       3  54  -53
12  18  -19      20   -   -7       1   -    4      1    -    5           5    -   -7        4  15  -16
14  70  -72      21  11   10       2   -   -4      2   21  -23           6   65  -60        5   -  -11
16  36   34                        3   -   -6      3   28   33           7    -    4        6  18   21
18  33  -34        5  0  L         4   -   12      4  117  101           8   76  -71        7  72  -67
20   -    7      1  56   55        5  27   23      5   35   35           9    -   15        8  29  -28
22   -   -5      2  10   11        6   -  -12      6   45  -45          10   37  -39        9   -    0
                 3  49   50        7   -    2      7   23   25          11    -    9       10   -   11
  1  0  L        4  19   19        8   -    3      8   26   27          12   36  -41       11  17  -18
 2  59   57      5  18   19        9   -    5      9   17   22          13    -   -6       12   -   -8
 3   8    9      6  19   19       10  14  -15     10   57  -55          14    -   16       13   -   13
 4  82   84      7   -  -12                       11    -    3         15    -    7       14   -    4
 5  15   15      8   -    1       11  0  L        12    -    6         16    -    3       15   -  -15
 6  36   42      9   -   -4       1    -   -2     13    -   -1         17    -    7       16  15  -15
 7   9   -9     10   -   -2       2    -    7     14   48  -44
 8  20   23     11  43  -45       3    -   -8     15    -    4           2  2  L           7  2  L
 9   -  -13     12   -   -9       4    -    8     16    -    5         0   77  -60       1  17   20
10  23   25     13   -  -12       5    -   -4     17    -  -11         1  108   99        2  16  -16
11   -  -12     14   -   -5       6   10   11     18    -  -15         2    -    4        3  18   22
12   -    8     15  15  -15                                           3  102  -92        4   -   -1
13   -   11     16   -   -8        0  1  L           5  1  L           4  104  100        5  16   18
14  25  -28     17   -    1       3  204  168     1    -   -1         5    -    6        6   -   10
15  10  -11     18   -   -4       5   16  -17     2   58   56         6   37  -39        7   -   -9
16  22  -26     19   -   -9       7  151  134     3   49  -45         7   72  -69        8   -   -2
17   -   -7     20   -   -6       9    -   -5     4   52   52         8    -  -10
18  18  -19                      11   82   77     5    -   -3         9   27   31          8  2  L
19   -   -1       6  0  L        13   46  -48     6   33   33        10   56  -52       0  20   24
20   9  -10      0  27   30      15    -    6     7    -    8        11   43  -42       1   -   13
21   -    5      1  27  -29      17   25  -28     8   41   40        12    -   -3       2   -   -9
22  11  -11      2  44  -44      19    -    6     9    -    8        13    -   13       3  22   29
                 3  31   32      21   22  -23    10    -    9        14   43  -40       4  22   26
  2  0  L        4   -    0                      11    -    3        15    -  -16
 0  87  -66      5  33   32        1  1  L        12    -    1        16   17  -18        9  2  L
 1  76  -79      6  46  -45      3   74  -68     13    -    4        17   18   24       1  18  -20
 2  14  -15      7  56   53      4   25   22     14    -   -9
 3  65   69      8  22   23      5   32  -33     15    -   13          3  2  L           0  3  L
 4 269 -252      9  11   13      6  111   95                        1   38   40       3 108 -114
 5  26   28     10  19  -21      7    -    2       6  1  L           2   25   26        5   -    3
 6  48   50     11   -    3      8    -   12     0   88  -80         3   28   26        7 106  -98
 7  43   44     12   -    8      9   24    8     1   39  -35         4   34   32        9   -   -4
 8  56  -57     13   -  -10     10   41  -41     2   18  -17         5   22   22       11  60  -59
 9  20  -21     14   -   -4     11   63   61     3   26   23         6   52   49       13  30   30
10  75   74     15   -    8     12    -   10     4   54  -53         7    -  -15       15   -   -7
11  32   33     16  19   20     13   22   22     5   27  -25         8   76   73       17  22  -20
12  18  -20     17  19  -16     14    -   -8     6   28   29         9   19  -21       19   -   -4
13  11  -14     18   -   -3     15   25   29     7    -   13        10   24   25       21  20   16
14  61   61                     16    -    0     8    -    1        11   15  -17
15   -   10       7  0  L       17    -    7     9   18  -21        12   16   15         1  3  L
16  17   16      1  32  -30     18    -   -2    10   30   31        13   16  -17       1  46   58
17  23  -24      2  27   25     19    -    6    11    -    7        14    -    1       2   -   -7
18  13   16      3  32  -29     20    -   -3    12    -   -5        15   17  -21       3  31   38
19   -    2      4   -    8     21    -   -5    13    -  -15        16    -    4       4  12  -16
20  13  -13      5  34  -30                     14   30   30        17    -   -3       5  19   18
21   -   -8      6   -    0       2  1  L                                              6  53  -54
                 7  11   11     0  106  -98       7  1  L             4  2  L          7   -  -10
  3  0  L        8   -   12     1   39   38     1    -    6        0   38  -40        8   -  -10
 1  63  -59      9   -   16     2   27   26     2    -   -9        1   45  -43        9  19  -19
 2  18  -21     10   -    4     3  133 -117     3    -  -14        2   29  -26       10  24   23
 3  31  -34     11  10   12     4   97  -91     4   19  -20        3  114  105       11  50  -45
 4   -    2     12   -    3     5    -   -5     5    -   -5        4   17   16       12   -   -7
 5  44  -44     13   9   11     6   34   35     6   25  -28        5   35  -36       13   -  -17
 6  35  -33     14   -   -5     7  130 -110     7    -   13        6    -    6       14   -    5
 7  20   21     15  17   18     8   19  -21     8   24  -25        7  127  108       15  22  -22
 8  50  -48     16   -    4     9    -    0     9    -   -4        8   26   26       16   -    0
 9  13   12                    10   75   73    10    -  -14        9   23  -22       17   -   -4
10  10  -10       8  0  L      11   55  -52    11    -    0       10   20   17       18   -    2
11  27   27      0  24  -22    12   13  -15    12    -  -10       11   55   54
12   -   12      1  33  -26    13   18   21    13    -   -2       12   31   28         2  3  L
13   -   12      2  34   31    14   19   20                      13   26  -28       0  67   72
14   -   10      3  17  -19    15    -   -3       8  1  L         14    -    7       1  21  -22
15  27   31      4  28  -28    16    -   -2    0   23   24        15    -    9       2  18  -21
16   -   12      5  18  -14    17  25   30     1    -   12        16   19   -3       3  83   82
17   -    0      6  23   24    18    -   16    2   18   19        17  19  -22       4  62   63
18  17   17      7   -   -7    19    -    5    3   31  -30                            5   -   12
19   -    3      8  10  -12    20    -  -12    4    -    7          5  2  L          6  29  -30
20  14   13      9  25  -21    21  13   13     5   18   21        1   36  -36       7  91   82
21   -  -10     10  19   19                    6    -    8        2    -  -18       8  15   17
                11   -  -12      3  1  L       7   20  -21        3   38  -37       9   -   -5
  4  0  L       12   -   -8    1  113   93     8    -    6        4   27  -28      10  57  -51
 0 153  125     13   -    3    2   53   49     9    -    8        5    -   -5      11  43   40
 1   -    2     14  15   15    3   18   18    10    -  -16        6   28  -30      12   -   12
 2  64   59     15  13   12    4   36  -36    11  15  -17        7    -    7      13   -  -12
 3  75  -72                    5   21   23    12  14  -18        8   18  -19      14  22  -18
 4  47   45       9  0  L      6   33  -34                       9   16   13      15   -    4
 5   -   10      1  32   28    7    -  -12       0  2  L        10    -  -14      16   -    2
 6   -    4      2   -    5    8   45  -46    2   10   13       11   34   33      17  22  -20
 7 100  -93      3   -    8    9    -  -10    4   88   67       12    -   -7
 8   -   -1      4  10  -10   10   15  -17    6   48   50       13    -   17        3  3  L
 9   -    7      5   -   -1   11   20  -23    8   37  -36       14    -   -5      1  48  -53
10  19  -20      6   9  -10   12    -  -11   10   87   79       15    -    8      2  20  -21
11  40  -39      7   -    5   13   31  -36   12   41   41       16    -    0      3  13  -11
12  20  -21      8   9  -10   14    -    4   14   49   46       17    -    3      4  27   28
13  22   23      9   -   -1   15    -  -17   16   20  -23                          5  14  -12
14   -  -13     10   -   -7   16    -    5   18   17   18                          6  24   26
                11  12  -13   17    -   -2
```

Table 3. Continued.

7	-	11
8	32	32
9	-	10
10	18	13
11	23	20
12	-	9
13	24	24
14	-	-4
15	-	13
16	-	-4

4 3 L

0	75	-76
1	-	-4
2	16	19
3	21	-22
4	77	-72
5	28	-29
6	39	36
7	22	-22
8	24	-23
9	20	-20
10	50	44
11	-	-5
12	-	-5
13	-	-2
14	39	33
15	-	-4

5 3 L

1	-	-1
2	35	-37
3	26	29
4	37	-37
5	-	1
6	27	-26
7	-	-8
8	31	-30
9	-	-8
10	-	-9
11	-	-3
12	-	-4
13	-	-4
14	-	6

6 3 L

0	56	59
1	26	26
2	-	9
3	19	-18
4	44	41
5	23	21
6	23	-22
7	-	-9

8	-	0
9	20	18
10	32	-25
11	-	-4
12	-	-2
13	-	12
14	30	-23

7 3 L

1	-	-3
2	-	7
3	-	12
4	-	17
5	-	0
6	22	22
7	-	-9
8	21	19
9	-	3
10	-	11

8 3 L

0	-	-18
1	-	-9
2	-	-13
3	21	22
4	-	-6
5	21	-16

0 4 L

2	-	-9
4	43	46
6	36	-38
8	64	63
10	64	-61
12	-	-11
14	44	-40
16	21	19
18	22	-19

1 4 L

2	19	25
3	-	8
4	35	39
5	-	8
6	26	27
7	-	-2
8	24	21
9	-	-6
10	15	14
11	-	-9
12	-	5
13	-	5
14	18	-15
15	-	-6
16	-	-14

2 4 L

0	45	-48
1	29	-36
2	-	-6
3	31	34
4	94	-113
5	-	6
6	27	27
7	35	33
8	21	-19
9	-	-11
10	44	40
11	20	17
12	-	-12
13	-	-9
14	42	34

3 4 L

1	27	-30
2	-	-9
3	15	-19
4	-	-10
5	18	-20
6	18	-21
7	-	13
8	22	-24
9	-	7
10	-	-6
11	-	15
12	-	5
13	-	7

4 4 L

0	56	61
1	-	7
2	30	27
3	45	-47
4	13	15
5	-	6
6	-	3
7	53	-47
8	-	4
9	-	2
10	-	-11
11	25	-23
12	-	-14

5 4 L

1	32	31
2	-	9
3	24	23
4	-	8
5	-	10

6	-	8
7	-	-5
8	-	1
9	-	-2
10	-	2
11	27	-25

6 4 L

0	15	18
1	-	-16
2	27	-25
3	21	18
4	-	0
5	18	19
6	24	-23
7	37	31
8	-	14

7 4 L

1	16	-17
2	-	12
3	16	-18
4	-	4
5	16	-16
6	-	-1

8 4 L

0	16	-13
1	16	-15
2	16	17
3	16	-12
4	16	-16
5	-	-8
6	14	15

9 4 L

1	16	16

0 5 L

3	50	62
5	9	-9
7	52	52
9	-	-4
11	33	31
13	25	-21
15	-	3
17	15	-15

1 5 L

1	28	-39
2	-	3
3	22	-28
4	8	8
5	14	-16

6	19	21
7	-	2
8	-	6
9	-	8
11	26	22
12	-	4
13	13	11
14	-	-2
15	14	13
16	-	0
17	-	3

2 5 L

0	31	-39
1	16	16
2	-	9
3	39	-45
4	30	-33
5	-	-1
6	15	16
7	44	-44
8	-	-9
9	-	4
10	27	25
11	25	-20
12	-	-6
13	13	11
14	14	11
15	-	-1
16	-	-1
17	14	14

3 5 L

1	33	33
2	-	5
3	15	15
4	17	-17
5	11	11
6	14	-13
7	-	-1
8	20	-17
9	-	-5
10	-	-6
11	11	-11
12	-	-5
13	13	-13
14	-	4
15	-	-7

4 5 L

0	47	44
1	-	0
2	-	-6

3	9	9
4	40	36
5	10	12
6	16	-18
7	11	11
8	12	14
9	-	8
10	27	-25
11	-	1
12	-	1
13	-	-2
14	20	-18

5 5 L

1	-	-4
2	19	18
3	20	-18
4	23	19
5	-	-5
6	16	14
7	-	2
8	21	17
9	-	3
10	-	4
11	-	1
12	-	3

6 5 L

0	36	-32
1	16	-15
2	-	-7
3	15	10
4	28	-23
5	13	-11
6	-	10
7	-	8
8	-	1
9	-	-9
10	15	13

7 5 L

1	-	5
2	-	-3
3	-	-5
4	-	-10
5	-	0
6	-	+12
7	-	7

8 5 L

0	12	11
1	-	6
2	12	10
3	16	-14

IR – SPECTRUM OF [Zn(N₃)₂(NH₃)₂]

The IR-spectrum of [Zn(N$_3$)$_2$(NH$_3$)$_2$], registered on a Beckman IR9 spectrophotometer, using the KBr technique, is reproduced in Fig. 3.

Fig. 3. Infra-red spectrum of [Zn(N$_3$)$_2$(NH$_3$)$_2$] (the monochromator was changed at 2000 cm^{-1}).

Table 4. Interatomic distances in $[Zn(N_3)_2(NH_3)_2]$ from two different determinations (A and B). Standard deviations in parentheses.

Superscript	Atom at
None	$x,\ y,\ z$
′	$1/2-x,\ 1/2+y,\ 1/2+z$
″	$-x,\ -y,\ -z$
‴	$1/2+x,\ y,\ 1/2-z$
⁗	$x,\ 1/2-y,\ z$

	Distance (Å)		
	A	B	Average
a) Zn−N distances within the coordination sphere			
Zn(1)−N(1)	2.039 (18)	2.029 (18)	2.034 (13)
Zn(1)−N(11)	1.998 (20)	2.014 (19)	2.006 (14)
Zn(1)−N(41)	1.974 (21)	2.000 (19)	1.987 (14)
Zn(2)−N(2)	2.002 (16)	1.996 (16)	1.999 (11)
Zn(2)−N(21)	1.953 (21)	1.979 (21)	1.966 (15)
Zn(2)−N(31)	2.006 (23)	1.978 (21)	1.992 (16)
b) N−N distances within the azide groups			
N(11)−N(12)	1.219 (40)	1.132 (38)	1.176 (28)
N(12)−N(13)	1.144 (41)	1.153 (40)	1.149 (29)
N(11)−N(13)	2.363 (38)	2.285 (36)	2.324 (26)
N(21)−N(22)	1.169 (35)	1.161 (29)	1.165 (22)
N(22)−N(23)	1.180 (39)	1.179 (33)	1.180 (26)
N(21)−N(23)	2.348 (36)	2.335 (33)	2.342 (24)
N(31)−N(32)	1.177 (34)	1.216 (35)	1.197 (24)
N(32)−N(33)	1.158 (35)	1.112 (35)	1.135 (25)
N(31)−N(33)	2.335 (36)	2.325 (33)	2.330 (24)
N(41)−N(42)	1.197 (33)	1.175 (33)	1.186 (23)
N(42)−N(43)	1.170 (37)	1.145 (36)	1.158 (26)
N(41)−N(43)	2.365 (37)	2.319 (34)	2.342 (25)
c) N···N distances forming edges of tetrahedra			
N(1)···N(11)	3.217 (24)	3.230 (23)	3.224 (17)
N(1)···N(41)	3 280 (22)	3.274 (21)	3.277 (15)
N(11)···N(41)	3.226 (30)	3.239 (28)	3.233 (21)
N(1)···N(1)⁗	3.481 (39)	3.496 (39)	3.489 (28)
N(2)···N(21)	3.261 (23)	3.278 (22)	3.270 (16)
N(2)···N(31)	3.237 (24)	3.197 (23)	3.217 (17)
N(21)···N(31)	3.165 (31)	3.189 (29)	3.177 (21)
N(2)···N(2)⁗	3.333 (33)	3.323 (34)	3.328 (24)
d) Selected N···N distances between different formula units			
N(1)···N(33)′	3.159 (24)	3.136 (24)	3.148 (17)
N(1)···N(41)‴	3.114 (22)	3.157 (21)	3.136 (15)
N(1)···N(21)″	3.183 (23)	3.170 (22)	3.177 (16)

Table 4. Continued.

N(1)···N(23)′	3.279 (25)	3.253 (26)	3.266 (18)
N(1)···N(13)‴	3.236 (25)	3.266 (24)	3.251 (17)
N(1)···N(33)″	3.309 (24)	3.367 (25)	3.338 (17)
N(2)···N(13)′	3.250 (25)	3.251 (23)	3.251 (17)
N(2)···N(11)‴	3.231 (23)	3.254 (21)	3.243 (16)
N(2)···N(31)″	3.286 (23)	3.279 (22)	3.283 (16)
N(2)···N(43)	3.268 (27)	3.284 (25)	3.276 (18)
N(2)···N(43)″	3.322 (27)	3.337 (25)	3.330 (18)
N(2)···N(23)″	3.327 (25)	3.357 (25)	3.342 (18)

Table 5. Angles in $[Zn(N_3)_2(NH_3)_2]$ from two different determinations (A and B). Notation as in Table 4.

	Angle (°)		
	A	B	Average
a) N − Zn − N angles within the coordination sphere			
N(1)−Zn(1)−N(11)	105.7 (0.5)	106.1 (0.5)	105.9 (0.4)
N(1)−Zn(1)−N(41)	109.6 (0.5)	108.7 (0.4)	109.2 (0.3)
N(11)−Zn(1)−N(41)	108.6 (1.0)	107.6 (0.9)	108.1 (0.7)
N(1)−Zn(1)−N(1)″″	117.2 (0.8)	119.0 (0.8)	118.1 (0.6)
N(2)−Zn(2)−N(21)	111.1 (0.5)	111.1 (0.5)	111.1 (0.4)
N(2)−Zn(2)−N(31)	107.8 (0.5)	107.1 (0.5)	107.5 (0.4)
N(21)−Zn(2)−N(31)	106.2 (1.0)	107.4 (0.9)	106.8 (0.7)
N (2)−Zn(2)−N (2)″″	112.7 (0.8)	112.7 (0.8)	112.7 (0.6)
b) Zn − N − N and N − N − N angles for the azide groups			
Zn(1)−N(11)−N(12)	130.0 (1.9)	133.9 (2.0)	132.0 (1.4)
Zn(1)−N(41)−N(42)	128.8 (1.7)	130.3 (1.6)	129.6 (1.2)
Zn (2)−N(21)−N(22)	126.7 (1.8)	125.3 (1.8)	126.0 (1.3)
Zn(2)−N(31)−N(32)	127.0 (1.9)	125.6 (1.8)	126.3 (1.3)
N(11)−N(12)−N(13)	177.8 (2.8)	179.5 (3.0)	178.7 (2.1)
N(41)−N(42)−N(43)	175.8 (2.5)	177.1 (2.5)	176.5 (1.8)
N(21)−N(22)−N(23)	177.1 (2.5)	172.1 (2.7)	174.6 (1.8)
N(31)−N(32)−N(33)	178.5 (2.5)	173.9 (2.6)	176.2 (1.8)
c) Selected Zn − N ··· N angles between different formula units			
Zn(1)−N(1)···N(33)′	95.6 (0.5)	96.8 (0.5)	96.2 (0.4)
Zn(1)−N(1)···N(41)‴	81.3 (0.6)	80.7 (0.6)	81.0 (0.4)
Zn(1)−N(1)···N(21)″	111.3 (0.6)	111.8 (0.5)	111.6 (0.4)
Zn(1)−N(1)···N(23)′	127.0 (0.6)	127.4 (0.6)	127.2 (0.4)
Zn(1)−N(1)···N(13)‴	75.0 (0.6)	75.1 (0.6)	75.1 (0.4)
Zn(1)−N(1)···N(33)″	154.0 (0.7)	152.2 (0.7)	153.1 (0.5)
Zn(2)−N(2)···N(13)′	93.0 (0.5)	93.2 (0.5)	93.1 (0.4)
Zn(2)−N(2)···N(11)‴	85.9 (0.6)	86.3 (0.6)	86.1 (0.4)
Zn(2)−N(2)···N(31)″	123.4 (0.6)	123.7 (0.6)	123.6 (0.4)
Zn(2)−N(2)···N(43)	80.0 (0.6)	79.9 (0.6)	80.0 (0.4)
Zn(2)−N(2)···N(43)″	109.0 (0.6)	108.7 (0.6)	108.9 (0.4)
Zn(2)−N(2)···N(23)″	152.7 (0.7)	152.4 (0.7)	152.6 (0.5)

When interpreting the spectrum, it should be borne in mind that the crystals prepared were not entirely free from mother liquor. The quantitative analyses indicated the presence of some oxygen compound, probably nitrate. This suggestion is supported by the IR-spectrum, where, besides those peaks due to the azide and ammine groups, there are peaks which might originate from nitrate.

An asymmetric azide group is expected to show a very strong band due to antisymmetric stretching just above 2000 cm^{-1} and a weaker band due to symmetric stretching around 1300 cm^{-1}. A weak band due to bending of the azide group is also expected just above 600 cm^{-1}.[25,26] In the spectrum registered for [Zn(N$_3$)$_2$(NH$_3$)$_2$], there is a strong split band with at least three peaks between 2110 cm^{-1} and 2060 cm^{-1} which can be attributed to antisymmetric azide stretching. The two other azide bands are more difficult to locate, because the ammine group and even nitrate absorb in partially the same regions. By comparison with the spectra of [Cu(N$_3$)$_2$(NH$_3$)$_2$][1] (Table 6)

Table 6. A comparison of the frequencies (cm^{-1}) of the IR peaks registered for [Cu(N$_3$)$_2$(NH$_3$)$_2$][1] and [Zn(N$_3$)$_2$(NH$_3$)$_2$]. In the regions marked with an asterisk, there is some ambiguity in the interpretation, owing to absorption by more than one group.

	[Cu(N$_3$)$_2$(NH$_3$)$_2$]	[Zn(N$_3$)$_2$(NH$_3$)$_2$]
NH$_3$ (stretch)	3340, 3260, 3200, 3180	3330, 3260, 3200, 3170
NH$_3$ (bend)	1600	1610
NH$_3$ (bend)	1240 *	1240 *
NH$_3$ (bend)	660 − 720 *	650 − 700 *
N$_3$ (stretch)	2080, 2040	2110, 2080, 2060
N$_3$ (stretch)	1290, 1340 *	1350 *
N$_3$ (bend)	610 *	610 *

and [Zn(N$_3$)$_2$(C$_5$H$_5$N)$_2$],[5] however, it seems possible that one of the peaks originating from the expected split symmetric stretching band may be the weak band at 1350 cm^{-1}, while the peak at 610 cm^{-1} may be assumed to be the bending band.

A coordinated ammine group is expected to show a strong absorption due to stretching below 3400 cm^{-1}. Hydrogen bonding causes the displacement of the band to lower frequencies, and there is a relation between the distance between the hydrogen bonded nitrogen atoms and the frequency of the absorption peak.[30] Other absorption bands due to bending of the ammine group are to be found around 1600 cm^{-1}, 1150 − 1350 cm^{-1}, and 600 − 800 cm^{-1}.[27] The split band registered for [Zn(N$_3$)$_2$(NH$_3$)$_2$], with peaks between 3330 cm^{-1} and 3170 cm^{-1}, may be assigned to the stretching modes of hydrogen bonded ammine groups, and the peak at 1610 cm^{-1} might be that due to asymmetric deformation. As mentioned previously, the regions 1150 − 1350 cm^{-1} and 600 − 800 cm^{-1} are, however, more difficult to interpret, because of azide and nitrate absorption, but by comparison with the IR-spectra of [Cu(N$_3$)$_2$(NH$_3$)$_2$][1] (Table 6) and [Zn(NH$_3$)$_4$]I$_2$,[27] the band at 1240 cm^{-1} may be attributed to the

symmetric deformation, while the broad absorption band between 650 cm^{-1} and 700 cm^{-1} is probably due to rocking of the ammine groups.

The two absorption bands which may originate from nitrate in the mother liquor are a band in the region just below 1400 cm^{-1}, probably that at 1380 cm^{-1}, and the narrow peak at 825 cm^{-1}.[27]

The IR-spectrum thus supports the conclusion that the compound investigated contains ammine groups and azide groups, probably asymmetric ones. The IR-spectrum indicates, moreover, that the adhering solidified mother liquor contains nitrate.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The zinc atoms are each surrounded by an approximately tetrahedral configuration of four nitrogen atoms (Fig. 4), two of which are end atoms of the azide groups, while the other two are the nitrogen atoms of the ammine ligands. The molecules of $[Zn(N_3)_2(NH_3)_2]$ are linked together by weak hydrogen bonds, the presence of which is indicated by relatively short $N-N$ distances and by the IR-spectrum.
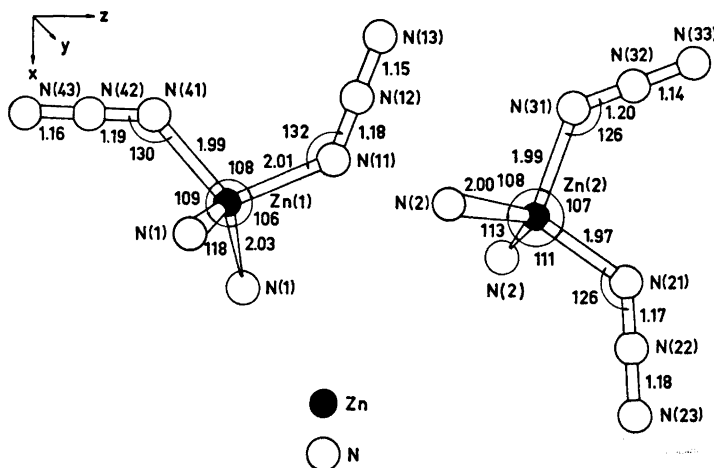
Fig. 4. The configuration of ligands about the two crystallographically different zinc atoms. Distances in Å, and angles in degrees.

The distances from the zinc atoms to the nitrogen atoms of the azide groups are: $Zn(1)-N(11)$ $2.00_6 \pm 0.01_4$ Å, $Zn(1)-N(41)$ $1.98_7 \pm 0.01_4$ Å, $Zn(2)-N(21)$ $1.96_2 \pm 0.01_5$ Å, and $Zn(2)-N(31)$ $1.99_2 \pm 0.01_6$ Å. The two ammine groups coordinated to each zinc atom are crystallographically equivalent, the $Zn-N$ distances being $Zn(1)-N(1)$ $2.03_4 \pm 0.01_3$ Å, and $Zn(2)-N(2)$ $1.99_9 \pm 0.01_1$ Å (Table 4). These $Zn-N$ distances are in agreement with other $Zn-N$ distances reported [28,29] and with those found in the compound $[Zn(N_3)_2(C_5H_5N)_2]$,[5] in which zinc is also tetrahedrally coordinated by four

nitrogen atoms, the four different $Zn-N$ distances lying between 1.93 ± 0.02 Å and 2.06 ± 0.02 Å.

There are four crystallographically different azide groups, all of which are bonded to one zinc atom through one of their end atoms. In accordance with previous investigations [1-6] this should give rise to asymmetric azide groups, with the longer nitrogen-nitrogen distance closer to the zinc—nitrogen bond. In the case of $[Zn(N_3)_2(NH_3)_2]$, the two data sets A and B yield average distances for the $N-N$ distance adjacent to the $Zn-N$ bond of 1.18 ± 0.03 Å, 1.17 ± 0.02 Å, 1.20 ± 0.02 Å, and 1.19 ± 0.02 Å, and for the other $N-N$ distance (azide groups in the same order): 1.15 ± 0.03 Å, 1.18 ± 0.03 Å, 1.14 ± 0.03 Å, and 1.16 ± 0.03 Å (Table 4). Although no statistical proof can be provided, it appears, however, reasonable to assume that all four azide groups are asymmetric, with the longer $N-N$ distance adjacent to the $Zn-N$ bond. It is also usually possible to detect the presence of an asymmetric azide group from the IR-spectrum, since the symmetric stretching band at approximately 1300 cm^{-1} appears only for asymmetric azide groups. In this case, however, the support offered by the IR-spectrum is not entirely reliable, since ammonia and nitrate absorb in the same region.

The azide groups are almost linear, the four $N-N-N$ angles lying between $175 \pm 2°$ and $179 \pm 2°$ (Table 5). The angles between the azide axis and the $Zn-N$ bond lie in the range $126 \pm 1°$ to $132 \pm 1°$.

All these distances and angles are in agreement with those found in other related compounds.[1-6]
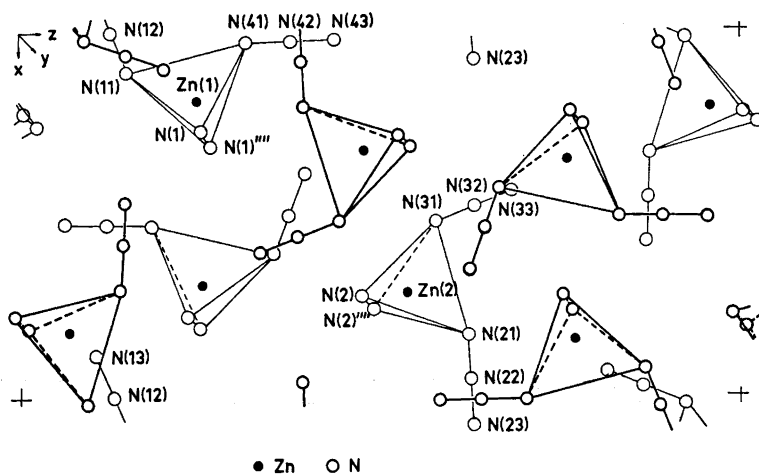
Fig. 5. Packing of the $[Zn(N_3)_2(NH_3)_2]$ molecules in the unit cell.

The tetrahedral units of $[Zn(N_3)_2(NH_3)_2]$ (Fig. 5) are joined together by hydrogen bonds of the type $N-H\cdots N$, as indicated by the IR-spectrum. According to Pimentel and McClellan,[30] the average $N-H\cdots N$ distance for such a bond is 3.10 Å, with a standard deviation of 0.13 Å (37 observations),

and a rather large deviation of the $N-H\cdots N$ bond from linearity may be possible.[33] Thus, in the structure of $[Zn(N_3)_2(NH_3)_2]$, each ammine group is in contact, at $N-H\cdots N$ distances of $3.14-3.34$ Å (cf. Tables 4d and 5c), with six nitrogen atoms belonging to azide groups. A similar situation was found in $[Cu(N_3)_2(NH_3)_2]$,[1] where the $N-H\cdots N$ distances from the nitrogen atom of the ammine group to four different nitrogen atoms of azide groups lie in the range $3.18-3.31$ Å. The weak hydrogen bonds in these compounds should thus not be pictured in terms of strictly directed bonds joining two atoms with the hydrogen atom lying between them, but rather as a general attraction, through hydrogen atoms, between the nitrogen atom of an ammine group and nitrogen atoms of several azide groups.

A discussion of $[Zn(N_3)_2(NH_3)_2]$ in the context of the related inorganic metal azides earlier investigated [1-6] will be published shortly.

All computer calculations, apart from those carried out in 1962, were performed on an IBM 360/50 computer at the Göteborg Universities' Computing Centre.

REFERENCES

1. Agrell, I. *Acta Chem. Scand.* **20** (1966) 1281.
2. Agrell, I. *Acta Chem. Scand.* **21** (1967) 2647.
3. Agrell, I. and Lamnevik, S. *Acta Chem. Scand.* **22** (1968) 2038.
4. Agrell, I. *Acta Chem. Scand.* **23** (1969) 1667.
5. Agrell, I. *Acta Chem. Scand.* **24** (1970) 1247.
6. Agrell, I. *Acta Chem. Scand.* **24** (1970) 3575.
7. Brosset, C. and Agrell, I. *Nature* **202** (1964) 1210.
8. Dennis, L. M. and Isham, H. *J. Am. Chem. Soc.* **29** (1907) 20.
9. Strecker, W. and Schwinn, E. *J. prakt. Chem.* **152** (1939) 207.
10. Lagowski, J. J. *The Chemistry of Non-Aqueous Solvents*, II, Academic, New York 1967, p. 328.
11. Gmelin, *Handbuch der anorg. Chemie*, 8th Ed., **22** (1938) 250, 315, 564.
12. Audrieth, L. and Kleinberg, J. *Non-Aqueous Solvents*, Wiley, New York 1953, p. 46.
13. Reuter, G. *Private communication from the Alfred Bernhardt Mikroanalytisches Laboratorium.*
14. Schwarzenbach, G. *Complexometric Titrations*, Methuen, London 1957, p. 83.
15. Arnold, J. W. *Ind. Eng. Chem. Anal. Ed.* **17** (1945) 215.
16. Kirsten, W. *Anal. Chem.* **24** (1952) 1078.
17. Danielsson, E. *Unpublished work.*
18. Belcher, R. and Wilson, C. L. *Inorganic Microanalysis*, Longmans, Green and Co., London 1957, p. 68.
19. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
20. Berggren, J. *To be published.*
21. Modified programmes in use at this Department. POWDER was originally written by Lindqvist, O. and Wengelin, F., DATA P2 by Coppens, P., Leiserowitz, L. and Rabinowich, D., DRF by Zalkin, A., LALS by Gantzel, R., Sparks, K. and Trueblood, K., and DISTAN by Zalkin, A.

22. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1959.
23. Tuvlind, S. O. *Fourierprogram 05 – 28. Private communication.*
24. Appel, K. *Strukturfaktorprogram KGK-1. Private communication.*
25. Gray, P. and Waddington, T. C. *Trans. Faraday Soc.* **53** (1957) 901.
26. Yoffe, A. D. *Develop. Inorg. Nitrogen Chem.* **1** (1966) 107.
27. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York 1963, pp. 92, 143, 149.
28. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London 1958.
29. Lumme, P., Lundgren, G. and Mark, W. *Acta Chem. Scand.* **23** (1969) 3011.
30. Pimentel, G. C. and McClellan, A. L. *The Hydrogen Bond*, Freeman, San Francisco 1960, pp. 87, 289.
31. Doyle, P. A. and Turner, P. S. *Acta Cryst.* **A 24** (1968) 390.
32. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
33. Hamilton, W. C. and Ibers, J. A. *Hydrogen Bonding in Solids*, Benjamin, New York 1968, p. 214.