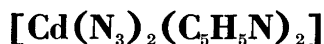


## The Crystal Structure of Diazidodipyridinecadmium



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 diazidodipyridinecadmium  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  has been determined by single crystal X-ray diffraction methods.

The crystals are tetragonal and belong to the space group  $I4_1/a$  (No. 88). The unit cell contains eight formula units and has the dimensions  $a=b=15.795 \pm 0.001$  Å,  $c=10.148 \pm 0.002$  Å, and  $V=2531.9$  Å<sup>3</sup>. The cadmium atom is octahedrally coordinated by six ligand nitrogen atoms at distances of  $2.336 \pm 0.017$  Å,  $2.349 \pm 0.012$  Å, and  $2.352 \pm 0.016$  Å. These octahedra are linked together by the azide groups to form a three-dimensional net. The azide groups are linear and appear to be symmetrical, the nitrogen-nitrogen distances being  $1.167 \pm 0.020$  Å and  $1.141 \pm 0.021$  Å.

The  $R$ -value of the proposed structure is 0.056.

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

A series of investigations of the crystal and molecular structures of a group of related inorganic metal azides is being performed by the author. Previously, 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>  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ ,<sup>4</sup> and  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>5</sup> have been determined, while the crystal structure of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  is described in this paper. A zinc-azide-ammine complex is now also being investigated.

The compound  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  was first prepared by Curtius and Rissom,<sup>6</sup> who described their product as colourless, blunt-shaped crystals, which rapidly turned yellow in air. Later, long, needle-shaped crystals of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  were prepared by Strecker and Schwinn<sup>7</sup> from  $[\text{CdCl}_2(\text{C}_5\text{H}_5\text{N})_2]$ ,  $\text{C}_5\text{H}_5\text{N}$ , and  $\text{NaN}_3$ .

## EXPERIMENTAL

*Preparation.* Crystals were prepared by several different methods, but those most suitable for a single crystal X-ray investigation were obtained by pouring stoichiometric amounts of first pyridine and then  $\text{NaN}_3$  into a 0.5 M solution of  $\text{Cd}(\text{NO}_3)_2$ . The precipitate

formed was dissolved in pyridine heated to about 80°. On cooling, colourless, pyramidal crystals, unstable in air, appeared.<sup>10</sup>

*Analysis.* The amount of cadmium in  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  was determined by titration with EDTA,<sup>8</sup> and the azide content by titration with a Ce(IV)-solution.<sup>9</sup> The following results were obtained: Cd 31.5,  $\text{N}_3^-$  22.0. Calc. for  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ : Cd 31.7,  $\text{N}_3^-$  23.7. The structure determination confirms, moreover, that  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  is the true formula of the product prepared.

### STRUCTURE INVESTIGATION

*X-Ray methods.* The single crystals of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ , used to collect the intensity data, were pyramidal, the crystallographic *c*-axis being perpendicular to the base of the pyramid. The dimensions of the basal plane were of the magnitude of  $0.18 \times 0.18$  mm, and the height of the pyramid was approximately 0.10 mm. Because the crystals were rather unstable in air, six different crystals had to be used.

Weissenberg photographs were registered for  $hk0-hk3$ ,  $hk5$ , and  $h0l$ , using  $\text{CuK}\alpha$ -radiation and multiple film equi-inclination techniques. Because of the large absorption with  $\text{CuK}\alpha$ -radiation ( $\mu = 155.1 \text{ cm}^{-1}$ ) a new set of equi-inclination Weissenberg photographs was taken for nine zones ( $hk0-hk8$ ) using Zr-filtered  $\text{MoK}\alpha$ -radiation ( $\mu = 18.4 \text{ cm}^{-1}$ ).

In order to determine accurate cell dimensions, X-ray powder photographs of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  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>22</sup> as an internal standard.

*Unit cell and space group.* From the Weissenberg photographs the crystals were seen to be tetragonal, belonging to the Laue group  $4/m$ . The approximate cell dimensions obtained from these photographs were refined using the Guinier photographs, the  $\sin^2\theta_{\text{obs}}$ -values being obtained from the measured *s*-values using the programme PEPP.<sup>11</sup> The refinement of the cell dimensions was performed with the programme POWDER<sup>12</sup> and the following values were obtained:  $a = b = 15.795 \pm 0.001 \text{ \AA}$ ,  $c = 10.148 \pm 0.002 \text{ \AA}$ , and  $V = 2531.9 \text{ \AA}^3$ . Observed and calculated  $\sin^2\theta$ -values are given, together with observed and calculated intensities, in Table 1.

A measure of the density of the crystals was obtained by the flotation method, using mixtures of  $\text{CHBr}_3$  and  $\text{C}_6\text{H}_5\text{Cl}$ . The density was determined to be  $2.0 \text{ g/cm}^3$ , which corresponds to eight formula units per unit cell ( $\rho_{\text{calc}} = 1.86 \text{ g/cm}^3$ ).

It was obvious from the X-ray photographs that the following general conditions were obeyed for all reflections:  $hkl : h + k + l = 2n$ ;  $hk0 : h = 2n$ ;  $00l : l = 4n$ . This is in accordance with space group  $I4_1/a$  (No. 88).<sup>22</sup>

*Determination of the structure.* The intensities of the reflections recorded both with  $\text{CuK}\alpha$ -radiation and with  $\text{MoK}\alpha$ -radiation 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>12</sup> No corrections were applied for absorption. There were thus serious absorption errors in the data collected with  $\text{CuK}\alpha$ -radiation ( $\mu R \approx 1.40$ ) and these data were therefore not used in the final calculations. Absorption errors in the data collected with  $\text{MoK}\alpha$ -radiation were, however, considered to be negligible ( $\mu R \approx 0.17$ ).

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

$hkl$	$10^6 \sin^2\theta_{\text{obs}}$	$10^6 \sin^2\theta_{\text{calc}}$	$I_{\text{obs}}$	$I_{\text{calc}}$ rel. scale
1 0 1	8162	8138	st	641
2 1 1}	17653	17650	st	580
1 2 1}				
2 2 0	19010	19024	st	625
3 0 1	27142	27162	rr	212
2 0 2	32510	32554	st	446
3 2 1}	36662	36674	st	295
2 3 1}				
2 2 2	42014	42066	st	310
4 1 1}	46186	46186	st	188
1 4 1}				
3 1 2	46770	46822	w	13
1 0 3	54247	54222	w	24
2 1 3}	63689	63734	w	64
1 2 3}				
5 0 1}	65189	65210	w	70
4 3 1}				
3 4 1}				
4 2 2}	70552	70602	st	340
2 4 2}				
2 5 1	74694	74722	m	127
4 4 0	76043	76096	m	100
3 2 3	82692	82758	m	124
0 0 4}	92260	92167	m	132
4 1 3}				
1 4 3}				
6 1 1}	93708	93746	w	49
1 6 1}				
6 2 0}	95141	95120	w	75
2 6 0}				
5 4 1}	103264	103258	m	113
4 5 1}				
6 0 2	108646	108650	m	99
2 2 4}	111247	111191	st	205
5 0 3}				
4 3 3}				
3 4 3}	112768	112770	w	39
6 3 1}				
3 6 1}	120756	120806	w	33
5 2 3}				
2 5 3}	122250	122282	w	34
7 0 1}				
4 0 4	130292	130216	w	45
7 2 1}	131764	131794	w	25
2 7 1}				
6 1 3}	139817	139830	w	45
1 6 3}				
6 4 2}	146714	146698	m	93
4 6 2}				
5 4 3}	149279	149342	w	29
4 5 3}				
6 5 1}	150837	150819	w	29
5 6 1}				

Table 1. Continued.

7 4 1 } 4 7 1 } 8 1 1 } 1 8 1 }	160350	160331	w	33
4 4 4 } 6 6 0 } 7 2 3 } 2 7 3 }	168223 171216 177820	168264 171216 177878	w w w	34 23 26
8 2 2 } 2 8 2 } 6 2 4 } 2 6 4 }	184729 187201	184746 187288	w w	65 68
8 4 0 } 4 8 0 } 7 6 1 } 6 7 1 } 9 2 1 } 2 9 1 }	190173 207909	190240 207891	w w	75 33
8 0 4 } 8 4 4 } 4 8 4 }	244379 282319	244360 282408	w w	37 24
10 4 2 } 4 10 2 }	298920	298891	w	29

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

Calculations were commenced using the set of intensity data available at that time, *i.e.* that recorded with  $\text{CuK}\alpha$ -radiation. A three-dimensional Patterson summation based on the reflections  $hk0-hk3$ , and  $hk5$ , was calculated, using the programme DRF.<sup>12</sup> Approximate scale factors for the different layers were obtained from a comparison of the common reflections in the  $hk0-hk3$ ,  $hk5$  layers, and the  $h0l$  layer.

On a closer examination of the films it was apparent that, apart for a few weak reflections, the following conditions of reflection were also obeyed for the layers with  $l$  even:  $hkl:h$ ,  $k=2n$  and  $h+k+l=4n$ . This is in accordance with the conditions of reflection for two of the eight-fold special positions in space group  $I4_1/a$ , both these positions requiring a centrosymmetrical point symmetry. The cadmium atom was therefore assumed to be situated in such a centro-symmetrical position. The origin was placed at the centre of symmetry at  $0, 1/4, 1/8$  from the inversion centre of the  $\bar{4}$ -axis, and the cadmium atom was assigned the eight-fold position  $8c$  with  $x=0, y=0$ , and  $z=0$ , which was in agreement with the largest peaks observed in the Patterson space.

Using the signs of the structure factors thus obtained, an electron density projection on (001) (*cf.* Fig. 1) and a three-dimensional electron density function were calculated. From the latter electron density distribution it was possible to locate the azide group, the nitrogen atoms of which were situated in the sixteen-fold position  $16f$ .

Using the approximate coordinates of these nitrogen atoms and with the known position of the cadmium atom, a three-dimensional difference electron density function was calculated. From geometrical considerations, assuming

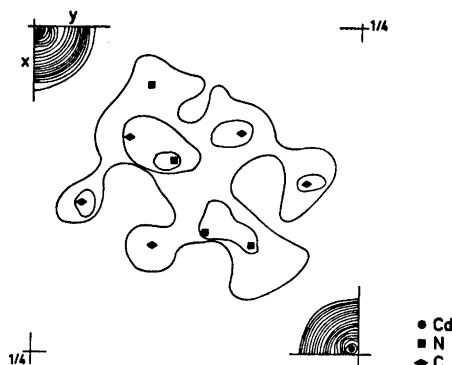


Fig. 1. Electron density projection of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  along the  $c$ -axis. Arbitrary units. Final positions of the atoms indicated.

an octahedral environment about the cadmium atom, the approximate coordinates of the nitrogen atom of the pyridine ring could be estimated. This position agreed well with a peak in the difference electron density distribution which was slightly higher than the others. The carbon atoms were then located in the difference electron density map, with the help of geometrical considerations, using the known dimensions of the pyridine ring.

Approximate coordinates were thus obtained for all ligand atoms, all of which are situated in the sixteen-fold position  $16f$ .

*Refinement of the structure.* The structural parameters were refined by means of least squares calculations using the programme LALS.<sup>12</sup> In the first stages of the refinement the data collected with  $\text{CuK}\alpha$ -radiation were used. Atomic coordinates and isotropic temperature factors were refined for all atoms, which entailed a total of 42 parameters. The refinement converged to give an  $R$ -value of 0.075 (289 independent reflections).

At this stage the intensity data from the  $hk0 - hk8$  layers (443 independent reflections), collected with  $\text{MoK}\alpha$ -radiation, were available. The final cycles of refinement, using the full matrix-programme, were therefore based on this set of data. All atoms were refined anisotropically, the relativistic Hartree-Fock X-ray scattering factors<sup>13</sup> were used, and Cruickshank's weighting scheme ( $w^{-1} = a + F_o + cF_o^2$ ) was employed with the constants  $a = 10.0$  and  $c = 0.015$ . The total number of parameters was 88. When the parameter shifts were less than 1 % of the standard deviations the refinement was terminated. The  $R$ -value was then 0.056, and a final difference electron density map showed no spurious peaks.

The resulting atomic parameters are given in Table 2, and observed and calculated structure factors are listed in Table 3. Distances and angles, calculated by the programme DISTAN,<sup>12</sup> are given in Tables 4 and 5.

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

The IR-spectrum of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ , registered on a Beckman IR 9 spectrophotometer, using the KBr technique, is shown in Fig. 2. Most of the bands originate from pyridine, but it is also possible to identify those bands

Table 2. Atomic coordinates (expressed as fractions of the cell edges) and anisotropic temperature factors of the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ . Standard deviations within parentheses. Space group  $I4_1/a$ .

Atom	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cd 8c	0.0000	0.0000	0.0000	0.0029 (01)	0.0029 (01)	0.0070 (02)	0.0000 (01)	-0.0000 (02)	-0.0010 (02)
N(1) 16f	0.0415 (10)	0.0926 (11)	0.1675 (16)	0.0043 (07)	0.0065 (09)	0.0085 (19)	-0.0030 (13)	-0.0014 (19)	-0.0052 (20)
N(2) 16f	0.1029 (08)	0.1121 (08)	0.2236 (13)	0.0034 (06)	0.0027 (05)	0.0050 (16)	-0.0006 (09)	0.0008 (14)	-0.0005 (12)
N(3) 16f	0.1625 (10)	0.1311 (10)	0.2800 (15)	0.0060 (09)	0.0045 (07)	0.0074 (23)	-0.0042 (13)	-0.0065 (19)	0.0042 (18)
N(4) 16f	0.1723 (08)	0.3303 (08)	0.4027 (12)	0.0034 (06)	0.0034 (06)	0.0035 (15)	-0.0005 (09)	-0.0011 (13)	-0.0002 (13)
C(1) 16f	0.2088 (11)	0.3772 (10)	0.4923 (23)	0.0042 (07)	0.0032 (06)	0.0140 (26)	0.0021 (11)	-0.0068 (26)	0.0006 (26)
C(2) 16f	0.1635 (12)	0.4233 (13)	0.5830 (19)	0.0055 (10)	0.0050 (09)	0.0059 (23)	0.0001 (15)	-0.0033 (22)	-0.0037 (21)
C(3) 16f	0.0738 (13)	0.4209 (13)	0.5793 (18)	0.0057 (10)	0.0060 (10)	0.0040 (23)	0.0034 (16)	0.0031 (23)	0.0023 (22)
C(4) 16f	0.0346 (12)	0.3714 (12)	0.4850 (20)	0.0049 (08)	0.0046 (08)	0.0099 (23)	0.0027 (13)	0.0037 (25)	0.0017 (25)
C(5) 16f	0.0869 (10)	0.3278 (11)	0.3984 (17)	0.0028 (06)	0.0044 (07)	0.0076 (22)	-0.0017 (11)	0.0017 (17)	0.0028 (19)

Table 3. Observed and calculated structure factors for [Cd(N<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>]. The columns are *k*, |*F*<sub>o</sub>|, and |*F*<sub>c</sub>|, respectively. Unobserved reflexions denoted by a dash.

2	K	0	13	66	72	10	-	31	3	K	2	6	-	-14	12	-	-15		
2	371	399	15	55	-60	12	-	28	1	75	76	8	95	98	14	116	112		
4	80	-83	17	33	36	14	48	50	3	-	25	15	K	2	16	-	12		
6	241	233	19	-	-25	16	-	34	5	-	18	3	-	18	18	62	61		
8	-	14	3	K	1	12	K	1	7	-	-16	1	-	5	29	-	-3		
10	157	166	2	150	141	1	87	-86	9	-	-40	5	-	-4	3	K	4		
12	-	2	4	129	117	3	95	98	11	-	0	11	-	0	1	-	21		
14	132	125	6	103	114	5	56	-52	13	-	13	13	-	13	3	-	8		
16	-	5	8	87	89	7	40	43	15	-	14	2	-	87	5	-	-11		
4	K	0	10	132	121	9	82	-83	4	K	2	5	0	K	3	9	-	41	
0	-	25	14	27	30	13	-	-16	2	290	279	5	168	162	11	-	10		
2	-	-37	16	52	54	15	33	40	4	-	42	7	221	-212	13	-	-32		
4	341	337	18	-	36	11	30	32	6	264	238	9	80	80	15	-	19		
6	-	-10	9	79	-87	12	-	29	8	-	9	11	73	-80	17	-	10		
8	287	275	4	K	1	2	41	42	10	168	165	10	168	165	15	-	-1		
10	-	14	1	224	-205	4	73	76	12	-	-33	4	1	K	3	4	K	4	
12	136	140	3	149	139	6	64	69	14	57	103	4	187	178	0	204	220		
14	-	-17	5	224	-206	8	42	42	6	189	175	6	189	175	2	-	15		
16	104	102	7	131	122	10	49	49	8	90	93	8	90	93	4	226	232		
0	-	45	9	79	-87	12	33	35	1	5	K	2	10	-	59	6	-	18	
2	238	235	11	73	70	14	-	29	3	-	-27	5	-	-6	6	-	159		
4	-	-18	13	52	-52	16	-	31	5	-	-8	7	-	-13	10	-	-8		
6	275	266	15	49	49	1	66	67	9	-	-2	5	54	-97	12	136	132		
8	-	15	17	-	30	3	46	-49	11	37	37	7	196	194	14	-	5		
10	210	202	19	-	30	5	52	52	13	-	-3	9	106	-106	16	86	87		
12	-	-10	2	-	0	7	54	-57	15	-	-18	11	-	78	18	-	0		
14	83	86	4	239	214	9	-	31	2	6	K	2	3	K	3	20	-	37	
0	181	201	6	166	159	11	44	43	2	277	245	2	342	279	1	5	K	4	
2	-	16	8	113	102	13	-	43	4	277	245	4	259	246	3	-	35		
4	260	242	10	80	81	15	31	35	6	-	-36	6	164	102	3	-	13		
6	-	8	12	71	70	2	31	35	8	196	178	8	81	91	5	-	-21		
8	200	188	14	45	49	4	-	32	10	-	-6	10	-	53	7	-	29		
10	-	-5	16	-	31	6	52	57	12	141	131	12	141	131	9	-	7		
12	-	67	18	37	36	8	35	38	14	-	-2	14	-	-2	11	-	-13		
14	-	7	10	-	34	10	-	34	1	7	K	2	1	4	K	3	13	-	1
0	-	-17	1	88	92	12	-	36	1	69	-77	3	170	161	15	-	7		
2	225	220	3	178	-147	3	-	36	3	-	22	5	212	-181	17	-	4		
4	-	11	5	111	103	1	-	-19	5	-	13	7	117	116	19	-	-1		
6	99	108	7	79	-76	3	43	48	7	-	-16	9	91	87	6	K	4	0	16
8	-	6	9	74	76	5	52	-53	9	-	32	2	170	149	2	275	268		
10	139	127	11	48	-47	7	36	40	11	-	2	4	152	148	4	-	-12		
12	-	-9	13	73	72	9	-	-26	13	-	-13	6	118	118	6	193	194		
0	168	175	15	58	-54	11	-	36	2	258	246	8	-	47	10	135	140		
2	-	-29	17	-	-27	2	46	48	4	-	-47	4	-	51	12	-	11		
4	136	127	4	72	65	4	32	36	6	151	185	6	134	-144	14	82	85		
6	-	26	6	76	73	6	-	27	8	-	16	1	134	-144	16	-	-6		
8	103	100	8	140	142	8	33	37	10	135	130	3	137	133	18	45	48		
10	-	-10	10	8	88	105	10	-	12	-	10	5	84	-88	7	-	13		
12	111	110	12	75	74	18	K	1	14	99	96	7	-	68	8	K	4	1	26
0	-	8	12	47	51	1	47	47	1	9	K	2	9	-	-70	3	-	13	
2	107	114	14	49	49	3	39	-44	3	-	7	2	7	K	3	5	-	23	
4	-	0	16	33	36	5	-	28	5	-	-3	4	-	53	7	43	-43		
6	152	140	18	-	27	7	-	-29	7	-	64	6	-	37	9	-	-19		
8	-	1	8	K	1	19	K	1	7	-	6	8	121	104	11	-	11		
0	-	-8	1	121	-126	2	-	30	9	-	-26	6	81	82	13	-	27		
2	107	114	3	83	89	4	39	37	11	-	-2	8	81	82	15	-	-4		
4	-	0	5	70	-69	6	-	26	13	-	-3	1	78	90	17	-	-5		
6	152	140	7	9	105	20	K	1	2	10	K	2	1	8	K	3	19	-	0
8	-	1	9	58	-54	1	37	-38	2	197	183	3	135	-128	5	8	K	4	276
0	-	93	11	81	80	1	37	-38	4	-	2	5	72	83	0	278	276		
2	-	19	13	73	-74	4	0	K	6	197	183	6	78	-78	2	-	6		
4	100	102	15	30	32	4	69	-50	8	136	129	8	-	88	4	169	156		
0	K	1	17	-	-32	4	278	288	10	-	22	2	104	104	6	-	133		
3	219	188	6	8	-	8	-	4	12	93	92	4	92	105	8	112	111		
5	-	-28	8	-	175	10	162	170	6	-	4	6	-	54	10	-	0		
7	198	181	2	177	175	10	162	170	11	K	2	11	K	3	12	124	118		
9	150	-144	4	54	58	12	-	13	1	-	-3	1	85	-91	14	-	-1		
11	48	50	6	76	80	14	116	134	3	-	3	3	104	111	16	49	44		
13	66	-63	8	78	76	16	-	4	5	-	8	7	-	28	18	-	0		
15	73	73	10	47	47	3	1	K	7	-	-15	9	-	-15	1	9	K	4	12
17	33	-40	12	58	59	5	52	-53	11	-	-10	11	11	K	3	1	-	12	
19	-	26	16	49	48	7	-	20	12	K	2	2	-	76	5	-	6		
0	163	153	9	-	37	9	-	37	4	149	150	4	1	K	4	7	-	-16	
2	-	19	1	85	88	11	-	-48	2	-	42	5	-	-29	9	-	-11		
4	143	131	3	55	-62	12	-	23	4	112	115	7	-	-47	11	-	19		
6	97	101	5	94	94	15	-	17	6	-	115	9	-	2	13	-	-1		
8	125	118	7	68	-75	17	-	4	8	100	98	11	-	24	15	-	-3		
10	72	72	9	80	82	2	K	2	10	100	98	13	-	23	17	-	3		
12	68	69	11	93	-95	2	309	311	1	13	K	2	15	-	-7	10	K	4	9
14	43	44	13	-	25	4	216	315	2	-	0	17	-	-7	3	-	6		
16	-	19	15	-	-14	6	-	-11	3	-	34	5	19	-	7	0	177	190	
18	-	29	17	-	27	8	203	202	5	-	-20	6	2	K	4	4	-	-16	
0	K	1	10	K	1	10	126	135	7	-	-9	2	230	251	6	97	92		
5	305	269	2	95	99	14	-	1	9	-	12	4	51	43	8	-	13		
7	154	-149	4	108	111	16	87	93	1	14	K	2	6	182	195	10	126	117	
9	67	63	6	71	67	2	-	0	2	-	0	8	-	0	12	-	-3		
11	85	-84	8	75	77	4	74	84	4	74	84	10	141	135	14	60	61		





Table 4. Interatomic distances in  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ . Standard deviations within parentheses. Numbers enclosed in square brackets indicate fractional atomic coordinates.

a) Cd—N distances within the coordination sphere				Distance Å
N(1)	[0.04, 0.09, 0.17]	—Cd	[0.00, 0.00, 0.00]	2.336 (17)
N(3)	[0.12, 0.09, 0.03]	—Cd	[0.00, 0.00, 0.00]	2.352 (16)
N(4)	[0.08, 0.08, -0.15]	—Cd	[0.00, 0.00, 0.00]	2.349 (12)
b) N—N distances within the azide groups				
N(2)	[0.10, 0.11, 0.22]	—N(1)	[0.04, 0.09, 0.17]	1.167 (20)
N(3)	[0.16, 0.13, 0.28]	—N(2)	[0.10, 0.11, 0.22]	1.141 (21)
N(3)	[0.16, 0.13, 0.28]	—N(1)	[0.04, 0.09, 0.17]	2.308 (22)
c) N—C and C—C distances within the pyridine ring				
C(1)	[0.21, 0.38, 0.49]	—N(4)	[0.17, 0.33, 0.40]	1.306 (24)
C(5)	[0.09, 0.33, 0.40]	—N(4)	[0.17, 0.33, 0.40]	1.350 (20)
C(2)	[0.16, 0.42, 0.58]	—C(1)	[0.21, 0.38, 0.49]	1.375 (28)
C(3)	[0.07, 0.42, 0.58]	—C(2)	[0.16, 0.42, 0.58]	1.417 (28)
C(4)	[0.03, 0.37, 0.49]	—C(3)	[0.07, 0.42, 0.58]	1.382 (28)
C(5)	[0.09, 0.33, 0.40]	—C(4)	[0.03, 0.37, 0.49]	1.389 (26)
d) Selected distances other than bond distances				
C(5)	[-0.09, 0.17, 0.40]	···N(1)	[0.04, 0.09, 0.17]	3.344 (23)
C(5)	[0.08, 0.16, -0.15]	···N(1)	[0.04, 0.09, 0.17]	3.442 (23)
C(4)	[-0.03, 0.13, 0.49]	···N(2)	[0.10, 0.11, 0.22]	3.439 (24)
C(1)	[0.29, 0.12, 0.01]	···N(3)	[0.16, 0.13, 0.28]	3.433 (27)
C(3)	[0.17, 0.18, 0.67]	···C(1)	[0.21, 0.38, 0.49]	3.704 (27)
C(2)	[0.33, 0.41, 0.83]	···C(2)	[0.16, 0.42, 0.58]	3.620 (20)
C(5)	[-0.09, 0.17, 0.40]	···C(5)	[0.09, 0.33, 0.40]	3.685 (32)

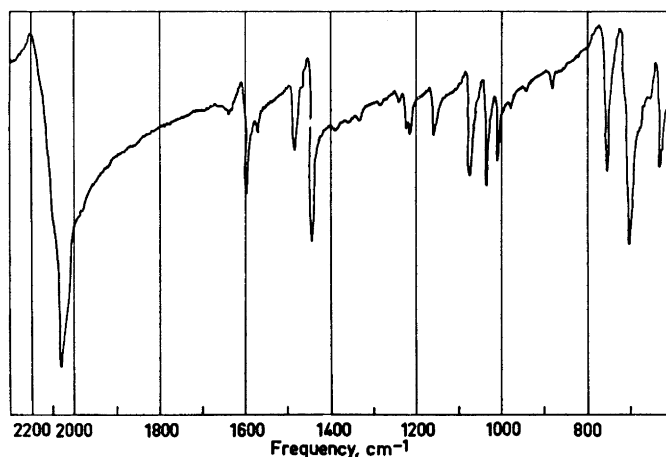


Fig. 2. Infrared spectrum of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ . (The monochromator was changed at  $2000\text{ cm}^{-1}$ .)

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

a) N—Cd—N angles within the coordination sphere

				Angle
N(1)[0.04, 0.09, 0.17]	—Cd[0.00, 0.00, 0.00]	—N(3)[ 0.12, —0.09, 0.03]		92.8 (0.6)
N(1)[0.04, 0.09, 0.17]	—Cd[0.00, 0.00, 0.00]	—N(3)[—0.12, 0.09, —0.03]		87.2 (0.6)
N(1)[0.04, 0.09, 0.17]	—Cd[0.00, 0.00, 0.00]	—N(4)[—0.08, —0.08, 0.15]		89.9 (0.5)
N(1)[0.04, 0.09, 0.17]	—Cd[0.00, 0.00, 0.00]	—N(4)[ 0.08, 0.08, —0.15]		90.1 (0.5)
N(3)[0.12, —0.09, 0.03]	—Cd[0.00, 0.00, 0.00]	—N(4)[—0.08, —0.08, 0.15]		92.2 (0.5)
N(3)[0.12, —0.09, 0.03]	—Cd[0.00, 0.00, 0.00]	—N(4)[ 0.08, 0.08, —0.15]		87.8 (0.5)

b) Cd—N—N and N—N—N angles for the azide groups

Cd [0.00, 0.00, 0.00]	—N(1)[0.04, 0.09, 0.17]	—N(2)[ 0.10, 0.11, 0.22]	138.9 (1.3)
Cd [0.25, 0.25, 0.25]	—N(3)[0.16, 0.13, 0.28]	—N(2)[ 0.10, 0.11, 0.22]	129.0 (1.3)
N(1)[0.04, 0.09, 0.17]	—N(2)[0.10, 0.11, 0.22]	—N(3)[ 0.16, 0.13, 0.28]	179.1 (1.7)

c) Angles within the pyridine ring

C(1)[0.21, 0.38, 0.49]	—N(4)[0.17, 0.33, 0.40]	—C(5)[ 0.09, 0.33, 0.40]	118.6 (1.4)
N(4)[0.17, 0.33, 0.40]	—C(1)[0.21, 0.38, 0.49]	—C(2)[ 0.16, 0.42, 0.58]	122.5 (1.6)
C(1)[0.21, 0.38, 0.49]	—C(2)[0.16, 0.42, 0.58]	—C(3)[ 0.07, 0.42, 0.58]	119.2 (1.8)
C(2)[0.16, 0.42, 0.58]	—C(3)[0.07, 0.42, 0.58]	—C(4)[ 0.04, 0.37, 0.49]	118.8 (1.8)
C(3)[0.07, 0.42, 0.58]	—C(4)[0.04, 0.37, 0.49]	—C(5)[ 0.09, 0.33, 0.40]	116.9 (1.7)
N(4)[0.17, 0.33, 0.40]	—C(5)[0.09, 0.33, 0.40]	—C(4)[ 0.04, 0.37, 0.49]	124.0 (1.6)

Table 6. Best least squares plane through the pyridine ring (Cartesian coordinates in Å) and deviations from this plane. Numbers in square brackets indicate position in Cartesian coordinates in Å.

$$-0.7797 X - 0.0071 Y - 0.6261 Z = -9.4204$$

Atom	Deviation Å
N(4)[ 9.166, 9.125, 3.525]	0.002
C(1)[ 9.907, 8.548, 2.615]	—0.002
C(2)[10.635, 9.264, 1.695]	0.002
C(3)[10.597, 10.681, 1.732]	—0.002
C(4)[ 9.815, 11.300, 2.689]	0.004
C(5)[ 9.126, 10.474, 3.568]	—0.004
Cd [ 7.898, 7.898, 5.074]	0.030

due to the azide group. An azide group is supposed to show a very strong band due to antisymmetric stretching ( $\nu_3$ ) just above  $2000 \text{ cm}^{-1}$  and a weaker band due to symmetric stretching ( $\nu_1$ ) around or a little above  $1300 \text{ cm}^{-1}$ . The symmetric stretching band vanishes in IR for symmetric azides. A weaker band due to bending ( $\nu_2$ ) of the azide group is also to be found just above  $600 \text{ cm}^{-1}$ .<sup>14,15</sup>

In the IR-spectrum of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  the strong antisymmetric azide stretching band is observed at  $2055 \text{ cm}^{-1}$ . There is no obvious peak due to symmetric stretching, and the weak band due to bending is a little difficult to

distinguish, because of the absorption of pyridine in this region, but a slightly split band at  $630\text{ cm}^{-1}$  might be due to overlap of a pyridine band with the bending band of the azide group.

The IR-spectrum will be discussed later, after the structure of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  has been described.

#### DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The cadmium atom in  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  is surrounded by an octahedral configuration of six nitrogen atoms (Fig. 3). Four of the surrounding nitrogen

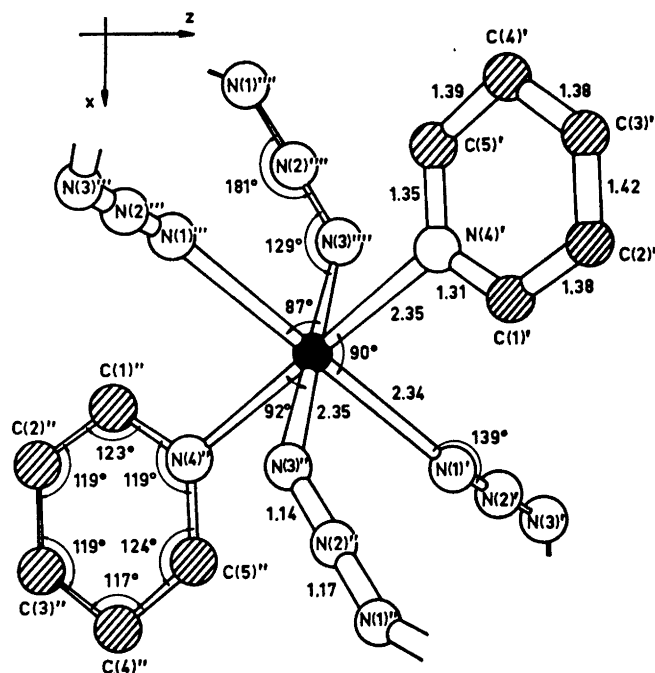


Fig. 3. The configuration around the cadmium atom in  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  as projected along the  $b$ -axis. Distances in Å.

atoms are end atoms of azide groups, while the other two are nitrogen atoms of pyridine rings. The distances from the cadmium atom to the nitrogen atoms of the azide groups are  $\text{Cd}-\text{N}(1)$   $2.336 \pm 0.017$  Å,  $\text{Cd}-\text{N}(3)$   $2.352 \pm 0.016$  Å and to the nitrogen atoms of the pyridine rings,  $\text{Cd}-\text{N}(4)$   $2.349 \pm 0.012$  Å (Table 4). An octahedral configuration of ligands is common in cadmium complexes, and in an approximate determination of the  $\text{Cd}-\text{N}$  distance in the octahedral complex  $\text{Cd}[\text{SC}(\text{NHCH}_2)_2]_2(\text{NCS})_2$  the value  $2.5 \pm 0.1$  Å is reported.<sup>16</sup>

There seems to be no difference in the distances between the cadmium atom and the nitrogen atoms of the two different ligands. In the azide-pyridine complexes investigated earlier,  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>4</sup> and  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N}_2)]$ ,<sup>5</sup> the bond lengths from the central atom to the nitrogen atoms of the azide ligands appeared to be shorter than those to the pyridine ligands. In the cadmium complex, however, the azide group is bonded equally within the limits of error to two cadmium atoms, one at each end, while in the copper and zinc complexes, the azide group is bonded principally to one central atom through one end.

The structure can be visualised as being built up by linking of the cadmium octahedra, through four corners, by azide groups, to form a three-dimensional network. The pyridine rings are attached to the two remaining corners of the octahedra (Fig. 4) and packed at van der Waals distances from the azide

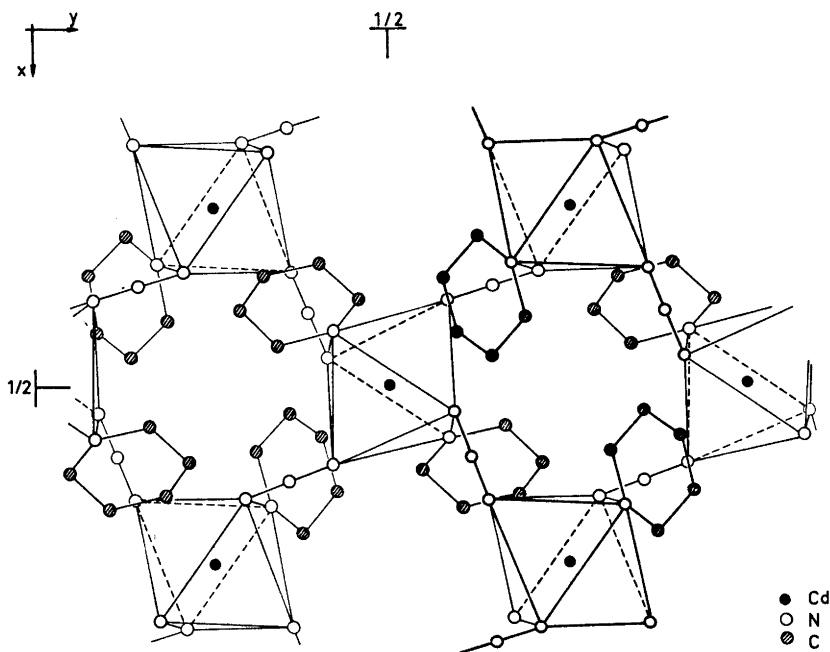


Fig. 4. A projection along the  $c$ -axis illustrating the coupling of the cadmium-nitrogen octahedra by azide groups, and the packing of the pyridine rings.

groups, the  $\text{C}\cdots\text{N}$  distances being 3.3 Å and 3.4 Å (Table 4). The rings are inclined to one another, the angle between the planes of two neighbouring rings being  $67^\circ$ , and the shortest distances between two carbon atoms of different rings being 3.6 Å.

The azide group appears to be linear and symmetrical, which is supported by the IR-spectrum. The nitrogen-nitrogen distances found are  $\text{N}(1)-\text{N}(2)$   $1.167 \pm 0.020$  Å and  $\text{N}(2)-\text{N}(3)$   $1.141 \pm 0.021$  Å (Table 4) and the

N(1)–N(2)–N(3) angle is  $179.1 \pm 1.7^\circ$  (Table 5). The azide group is coordinated at each end to a different, approximately equally remote cadmium atom.

It appears natural that an azide group which is coordinated equally at both ends is symmetric, whereas an azide group which is not coordinated equally at both ends tends to be asymmetric, and that the longer nitrogen–nitrogen distance is that corresponding to the end in which the azide is most strongly bonded.<sup>21</sup> This is illustrated in Fig. 5, which shows, schematically,

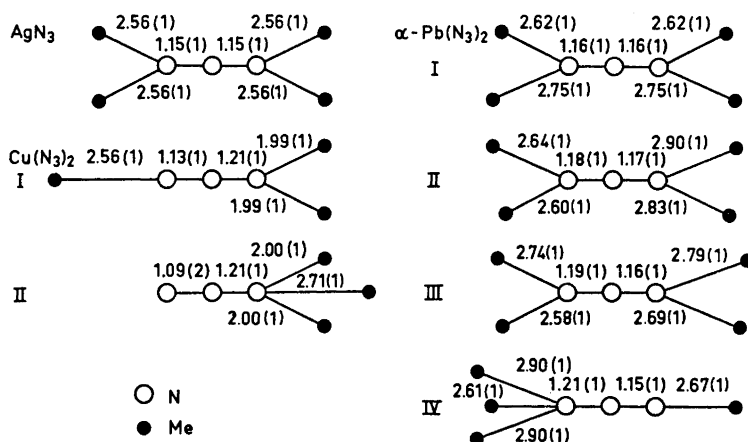


Fig. 5. Schematic illustration of the coordination of the azide groups and the bond lengths in three explosive metal azides.

the coordination of the azide group and the bond lengths in three different azides of heavy metals, and it may be noticed, that they are all three explosive, although both symmetric and asymmetric azide groups are represented among them. In AgN<sub>3</sub>,<sup>17,23</sup> for instance, the azide group is equally coordinated at both ends and was found to be symmetric. In Cu(N<sub>3</sub>)<sub>2</sub>,<sup>3</sup> however, both azide groups are coordinated differently at each end and were found to be asymmetric, the degree of asymmetry being related to the difference in strength of the bonds to the metal atoms. In α-Pb(N<sub>3</sub>)<sub>2</sub><sup>18</sup> both symmetric and asymmetric azide groups are present, and a similar relationship between asymmetry and bonding of the azide group is found. In the azide complexes investigated earlier by the author<sup>1,2,4,5</sup> the azide groups have all been coordinated unequally at both ends and have been found to be asymmetric.

The angle between the Cd–N bond and the azide axis is  $139 \pm 1^\circ$  at N(1) and  $129 \pm 1^\circ$  at N(3). The corresponding values reported are generally around  $120^\circ$ , though they vary over a wide range, and values even larger than those found in [Cd(N<sub>3</sub>)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>N)<sub>2</sub>] have been reported in cases where the azide group is strongly coordinated at more than one end, e.g. α-Pb(N<sub>3</sub>)<sub>2</sub>.<sup>18</sup>

The pyridine ring is planar, within the limits of error, and the best plane through the atoms of the ring was obtained by least squares calculations,

using the programme PLANEFIT<sup>12</sup> (Table 6). Distances and angles within the ring (Tables 4 and 5) are in agreement with those found in the structures of  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>4</sup> and  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>5</sup> and those reported for pure pyridine.<sup>19,20</sup>

The two pyridine rings coordinated to the same central atom are coplanar, owing to symmetry reasons, and the central cadmium atom is situated approximately in the plane of the pyridine rings, the perpendicular distance from the plane of the rings to the cadmium atom being 0.03 Å. The plane of the pyridine ring is inclined at angles of 43° and 44°, respectively, to the two square planes in the octahedron containing the central cadmium atom and the nitrogen atoms of the pyridine rings, *i.e.* the planes through the nitrogen atoms N(4)', N(4)", N(1)', and N(1)''' and the nitrogen atoms N(4)', N(4)", N(3)", and N(3)'''' (cf. Fig. 3). A similar rotation of the plane of the pyridine ring was observed in  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ , where the inclination was 43° with respect to the plane containing the central copper atom and its four nearest nitrogen atoms.

A comparison of the IR-spectrum of  $[\text{Cd}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$  with those of  $[\text{Cu}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>4</sup> and  $[\text{Zn}(\text{N}_3)_2(\text{C}_5\text{H}_5\text{N})_2]$ <sup>5</sup> reveals a close agreement between absorbing frequencies, but it is also possible to detect differences in the spectra due to structural inequalities between the three complexes.

Thus, in the cadmium complex the pyridine rings, as well as the azide groups, are crystallographically equivalent, and the azide group is bonded in both ends at approximately equal distances to two different cadmium atoms. In the copper complex the pyridine rings are crystallographically equivalent, while the two azide groups are crystallographically independent. The azide groups are differently coordinated, but both are bonded more strongly to one copper atom at one end. Finally, in the zinc complex, both the two pyridine rings and the two azide groups are crystallographically different, and the azide groups are bonded to one zinc atom in one end only.

When examining the peaks originating from the pyridine ligands in the IR-spectra of the three compounds, it is found that they occur at almost exactly the same frequencies. In the spectrum of the zinc complex, however, most of the pyridine peaks are split, which is not observed in the spectra of the other two compounds.

The strong antisymmetric stretching band ( $\nu_3$ ) of the azide group is in all three compounds observed between 2100  $\text{cm}^{-1}$  and 2030  $\text{cm}^{-1}$ . Owing to the structures of the complexes, it is expected to be split for the copper and zinc complexes but not for the cadmium complex, this is supported by the spectra, except that for the copper complex the band appears as a single, although slightly broadened band.

The symmetric azide stretching band ( $\nu_1$ ) is registered between 1350  $\text{cm}^{-1}$  and 1330  $\text{cm}^{-1}$  in the copper and zinc compounds and, as expected, it is split for both compounds. The symmetric stretching is not observed for the cadmium complex, which is in accordance with its symmetrical coordination.

A very weak bending band ( $\nu_2$ ) is, for all three compounds, found in the region 630–610  $\text{cm}^{-1}$ .

All computer calculations have been performed on an IBM 360/50 computer at the Göteborg Universities' Computing Centre.

*Acknowledgements.* I wish to thank Professor Cyrill Brosset for all the facilities put at my disposal. I also wish to express my thanks to Professor Georg Lundgren and Professor Nils-Gösta Vannerberg for their encouragement and most helpful advice. Many thanks are due to Fil. mag. Birgitta Svensson for valuable assistance, to Mrs. Margareta Biéth for skilful help with the collection of the data, and to Dr. Susan Jagner for revising the English text of this paper.

Financial support in the form of grants from the *Swedish Natural Science Research Council* (Contract No. 2286-14), *Ograderade forskares fond*, and *Chalmers University of Technology*, the last to cover the costs of the computer work, is gratefully acknowledged.

## 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. Curtius, T. and Rissom, J. *J. prakt. Chem.* [2] **58** (1898) 294.
7. Strecker, W. and Schwinn, E. *J. prakt. Chem.* **152** (1939) 213.
8. Schwarzenbach, G. *Die komplexometrische Titration*, Ferdinand Enke, Stuttgart 1956, p. 78.
9. Arnold, J. W. *Ind. Eng. Chem. Anal. Ed.* **17** (1945) 215.
10. Svensson, B. *Unpublished work.*
11. Berggren, J. *To be published.*
12. 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.; DISTAN by Zalkin, A.; and PLANEFIT by Wengelin, F.
13. Doyle, P. A. and Turner, P. S. *Acta Cryst.* **A 24** (1968) 390.
14. Gray, P. and Waddington, T. C. *Trans. Faraday Soc.* **53** (1957) 901.
15. Yoffe, A. D. *Developments in Inorganic Nitrogen Chem.* **1** (1966) 107.
16. *Tables of Interatomic Distances and Configuration in Molecules and Ions*, The Chemical Society, London, Suppl. 1956-1959.
17. Hughes, E. W. *Personal communication* to Söderquist, R. (1966).
18. Choi, C. S. and Boutin, H. P. *Acta Cryst.* **B 25** (1969) 982.
19. Bak, B., Hansen, L. and Rastrup-Andersen, I. *J. Chem. Phys.* **22** (1954) 2013.
20. Liquori, A. M. and Vacicgo, A. *Ric. Sci.* **26** (1956) 1848.
21. Griffith, W. P. *Developments in Inorganic Nitrogen Chem.* **1** (1966) 265.
22. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1959.
23. Söderquist, R. *Symp. Chem. Probl. Connected Stabil. Expl.* 1st Ed., Hansson, J., Stockholm 1967.

Received April 23, 1970.