ACTA CHEMICA SCANDINAVICA 23 (1969) 3011–3022

The Crystal Structure of Zinc Picolinate Tetrahydrate, $Zn(C_6H_4O_2N)_2(H_2O)_4$

PAAVO LUMME, GEORG LUNDGREN and WANDA MARK

Department of Chemistry, University of Jyväskylä, Finland, and 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 zinc picolinate, $Zn(C_6H_4O_2N)_2(H_2O)_4$, has been determined by X-ray analysis. The monoclinic cell, which belongs to the space group $P2_1/c$, contains two formula units and has the dimensions $a=9.724$ Å, $b=5.221$ Å, $c=17.429$ Å, and $\beta=124.02°$.

The positions of the zinc atom and seven of the light atoms were obtained from Patterson projections, while the remaining atoms were located from electron density projections. The parameters were refined by anisotropic three-dimensional least squares calculations using a total of 845 independent intensities from two combined series of reflexions. A final R value of 0.116 was obtained.

The zinc atom is octahedrally coordinated by two oxygen and two nitrogen atoms lying in a plane, and two other oxygen atoms, situated above and below this plane. The octahedron is somewhat distorted, the Zn–N distances being 2.10 Å and the Zn–O distances 2.08 and 2.18 Å.

The molecules are assumed to be coupled together by hydrogen bonding. In the z direction hydrogen bonding occurs *via* an interjacent water molecule and in the y direction between two neighbouring molecules.

In connection with investigations on zinc picolinate complexes in aqueous solution it was suggested that zinc picolinate probably had a planar *trans* structure.[1] We therefore thought it would be interesting to study the complex in greater detail and thus decided to perform an X-ray investigation of the solid zinc picolinate.[2]

EXPERIMENTAL

The colourless crystals of zinc picolinate, $Zn(C_6H_4O_2N)_2(H_2O)_4$, were prepared according to a method described in previous papers.[3] Crystals were mounted with (010) and (100) as rotation axes and Weissenberg photographs ($h0l-h3l$,$0kl-5kl$) were taken using Cu$K\alpha$ radiation and multiple film techniques. The intensity scale, with which the intensities of the reflexions were visually compared, was made by making timed exposures of selected reflexions from the actual crystals.

The crystals were found to be monoclinic with the approximate cell dimensions, as determined from rotation and Weissenberg photographs:

$$a = 9.9 \text{ Å} \qquad b = 5.3 \text{ Å} \qquad c = 17.6 \text{ Å} \qquad \beta = 123°.$$

More accurate cell dimensions were calculated from a Guinier powder photograph using KCl as an internal standard (Cu$K\alpha_1$ radiation, $\lambda = 1.54050$ Å, $a_{KCl} = 6.2919_4$ Å at 20°C [4]). The reflexions were indexed and the cell constants were refined using the ALGOL program XALG POWDER,[5] the following cell dimensions and standard deviations being obtained:

$a = 9.7237 \pm 0.0019$ Å
$b = 5.2205 \pm 0.0013$ Å
$c = 17.4287 \pm 0.0031$ Å
$\beta = 124.015 \pm 0.013°$
$V = 733.3$ Å^3

The observed and calculated values of $\sin^2\theta$ less than 0.125 are listed in Table 1.*

From the cell volume and the experimental density of 1.688 g/cm^3, as determined from the loss of weight in benzene, there are $2.07 \cong 2$ formula units of $Zn(C_6H_4O_2N)_2(H_2O)_4$ in the unit cell. The following reflexions are systematically absent:

$h0l$ with $l = 2n+1$
$0k0$ » $k = 2n+1$

which is characteristic for space group $P2_1/c$.[6]

POSITIONS OF THE ATOMS

Since there are only two formula units in the unit cell the zinc atoms must be situated at centres of symmetry and thus occupy one of the 2-fold positions in $P2_1/c$. They were therefore arbitrarily assigned the position $P2_1/c$: 2(*a*). Since the remaining atoms must all occupy the 4-fold position 4(*e*), the interatomic vectors between the Zn and the C, N, and O atoms are: $\pm(x,\pm y,z)$ and $\pm(\bar{x},1/2\pm y,1/2-z)$.

The intensities were corrected for Lorentz and polarization effects, but no correction was made for absorption, since the linear absorption coefficient for Cu$K\alpha$ radiation is less than 32 cm^{-1}.

From the resulting $|F_o|^2$ data the Patterson projections $P(upw)$, $P(pvw)$ and a generalized Patterson function $P_1(uw)$ were calculated. The projection $P(upw)$ yielded eleven peaks, ten of which were of about the same height (*cf.* Table 2 and Fig. 1), and $P(pvw)$ showed eight peaks (*cf.* Table 2 and Fig. 2). It was possible to identify the peaks I and XI of the projection $P(upw)$ in $P(pvw)$ and $P_1(uw)$, shown in Fig. 3, and thus to determine their *v*-coordinates.

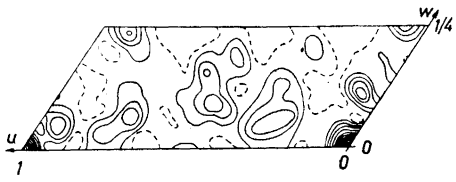

Fig. 1. Patterson projection $P(upw)$ of $Zn(C_6H_4O_2N)_2(H_2O)_4$.

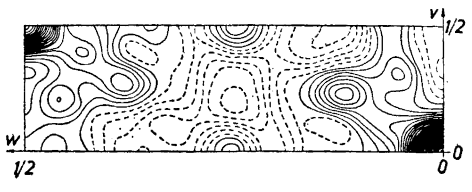

Fig. 2. Patterson projection $P(pvw)$ of $Zn(C_6H_4O_2N)_2(H_2O)_4$.

* The calculations were, however, based on reflexions with $\sin^2\theta$ values up to 0.250.

Table 1. Powder photograph of $Zn(C_6H_4O_2N)_2(H_2O)_4$. Cu$K\alpha_1$ radiation. $\lambda = 1.54050$ Å.

$h\ k\ l$	$10^5\sin^2\theta$ calc.	$10^5\sin^2\theta$ obs.	F calc.	I obs.
1 0 −2	910	909	70	st
1 0 0	913		55	
0 0 2	1137	1134	117	st
0 1 1	2461	2463	79	m
2 0 −2	2510		13	
1 1 −1	2804	2805	50	vw
1 1 −2	3087	3087	10	vvw
1 1 0	3090		40	
1 0 −4	3181	3169	93	w
1 0 2	3191		43	
0 1 2	3314	3308	35	vvw
2 0 −4	3641	3654	16	vvw
2 0 0	3653		66	
1 1 −3	3938	3944	107	st
1 1 1	3945		3	
0 1 3	4735	4725	35	vvw
2 1 −3	4968	4981	16	m
2 1 −1	4974		88	
1 1 −4	5358	5359	68	w
1 1 2	5368		50	
2 1 −4	5818	5821	64	w
2 1 0	5830		38	
1 1 −5	7347	7347	114	m
1 1 3	7359		23	
1 0 −6	7727	7721	31	vvw
1 0 4	7742		79	
3 1 −4	8104	8089	16	vvw
3 1 −2	8113		17	
3 0 0	8220	8219	67	vvw
3 1 −5	8952	8949	61	vw
3 1 −1	8971		44	
2 1 −6	9223	9249	5	vvw
2 1 2	9248		2	
0 1 5	9284		36	
1 2 −2	9618	9624	14	vvw
1 2 0	9621		32	
1 1 −6	9904	9909	41	vvw
1 1 4	9919		34	
3 1 −6	10369	10369	37	vvw
3 1 0	10397		34	
4 0 −6	11165	11191	13	vw
4 0 2	11189		46	
2 2 −2	11218		11	
2 2 −3	11499	11503	17	vvw
2 2 −1	11505		17	
1 2 −4	11889	11896	81	vw
1 2 2	11898		20	
2 2 −4	12349	12347	73	vvw
3 1 −7	12354		20	
2 2 0	12361		13	
4 1 −5	12495	12494	61	vwv
4 1 −3	12507		49	

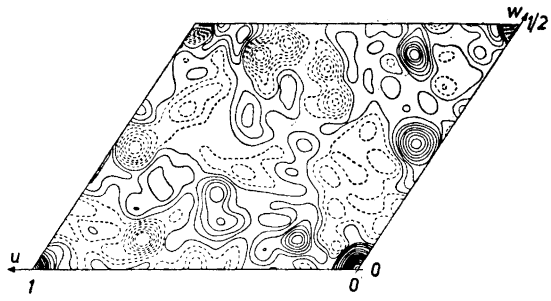

Fig. 3. Generalized Patterson projection $P_1(uw)$ of $Zn(C_6H_4O_2N)_2(H_2O)_4$.

The projection $P(pvw)$ suggested $v=0.23$ for peak I (height 372) in $P(upw)$ and the height of this peak in $P_1(uw)$ is -50, which corresponds to $372 \cos 2\pi v = -50$, *i.e.* $v=\pm 0.27$. Peak XI with height 306 in $P(upw)$ and -500 in

Table 2. Peaks in the Patterson projections $P(upw)$ and $P(pvw)$.

$P(upw)$				$P(pvw)$			
No.	u	w	height	No.	v	w	height
I	0.072	0.114	372	A	0.230	0.118	666
II	0.258	0.062	285				
III	0.319	0.045	242	B	0.308	0.054	320
IV	0.497	0.089	270				
V	0.731	0.065	287				
VI	0.788	0.033	180				
VII	0.944	0.052	274	C	0.204	0.456	404
VIII	0.305	0.204	40				
IX	0.522	0.184	140				
X	0.586	0.154	210	D	0.500	0.350	120
				E	0.273	0.383	487
XI	0.918	0.243	306	F	0.500	0.250	390
				G	0.000	0.250	150
				H	0.400	0.431	519

$P_1(uw)$ thus has $v=0.5$, which is confirmed by peak F in $P(pvw)$. $P(pvw)$ shows no well-defined maximum for $w=0.062$ corresponding to peak II in $P(upw)$ while $P_1(uw)$ shows a maximum with height 350; hence v cannot be determined. Correlation of III with B gives $v=0.31$ but according to $P_1(uw)$, which shows a peak of height 100, $v=0.18$ and v must therefore lie within the limits $0.18<v<0.31$. Peak IV corresponds to two broad maxima with $0.08<v<0.34$ and $0.67<v<0.92$ in $P(pvw)$ while $P_1(uw)$ shows a maximum of height 200 and, accordingly, $v=\pm 0.12$. Peak V corresponds to two undefined maxima in $P(pvw)$ with $0.17<v<0.83$. The corresponding maximum in $P_1(uw)$ at $u=0.269$, $w=0.435$ has a height of 350 so that it is, moreover, not possible to determine the v coordinate for this vector. Several maxima are obtained in $P(pvw)$ with $w=0.45$ as in VII, but since the maximum in $P_1(uw)$ at $u=0.056$, $w=0.448$ has a height of 100, $v=\pm 0.19$ and the corresponding maximum in $P(pvw)$ must be C with $v=0.20$. The interatomic distance between this atom and Zn is thus 1.7 Å but ought not to be less than ~2.0 Å according to previous reports.[7] The following positions for some of the light atoms were thus obtained from the Patterson projections:

4 X_{XI}	in 4(e):	$x = 0.082$	$y = 0$	$z = 0.257$
4 X_I	» 4(e):	$x = 0.072$	$y = 0.25$	$z = 0.114$
4 X_{II}	» 4(e):	$x = 0.258$	—	$z = 0.062$
4 X_{IV}	» 4(e):	$x = 0.497$	$y = \pm 0.12$	$z = 0.089$
4 X_{VII}	» 4(e):	$x = 0.056$	$y = \pm 0.20$	$z = 0.448$
4 X_{III}	» 4(e):	$x = 0.319$	—	$z = 0.045$
4 X_V	» 4(e):	$x = 0.269$	—	$z = 0.435$

where ± 0.12 means either $+0.12$ or -0.12.

$F_o(h0l)$ values were used together with the positions of these seven atoms and Zn to calculate a $\varrho(xpz)$ projection. The peaks VIII and IX in $P(upw)$ were not taken into account in this preliminary calculation, since there are negative minima in $P(pvw)$ for the w values in question. Nor were the remaining two peaks VI and X included because of the doubtful agreement between $P(pvw)$ and $P_1(uw)$. Peak VI corresponds to a maximum in $P(pvw)$ for which $0.125<v<0.875$ but there is no corresponding peak in $P_1(uw)$. The v value obtained from $P_1(uw)$ at $u=0.414$, $w=0.346$ for peak X is ± 0.38 since the height of the peak is -150, but the corresponding v value from the $P(pvw)$ peaks D and E is $v=0.50$ or $v=0.27$.

From the $\varrho(xpz)$ projection the x and z coordinates of the remaining four atoms were found, two of which were in good agreement with the peaks VI and X in $P(upw)$. In addition, the identities of all X atoms but two were determined. The complete identification was obtained from a second $\varrho(xpz)$ projection, which also verified our earlier conclusions. Approximate y coordinates were then obtained from a $\varrho(pyz)$ projection, the light atoms thus being found to occupy the preliminary positions:

4 C_1	in	$P2_1/c$:	4(e)	with	$x = 0.500$	$y = 0.121$	$z = 0.079$
4 C_2	»	»	»	»	$x = 0.313$	$y = 0.179$	$z = 0.042$
4 C_3	»	»	»	»	$x = 0.213$	$y = 0.330$	$z = 0.458$
4 C_4	»	»	»	»	$x = 0.404$	$y = 0.500$	$z = 0.350$
4 C_5	»	»	»	»	$x = 0.342$	$y = 0.750$	$z = 0.150$
4 C_6	»	»	»	»	$x = 0.483$	$y = 0.250$	$z = 0.321$
4 O_1	»	»	»	»	$x = 0.079$	$y = 0$	$z = 0.254$
4 O_2	»	»	»	»	$x = 0.079$	$y = 0.221$	$z = 0.117$
4 O_3	»	»	»	»	$x = 0.054$	$y = 0.250$	$z = 0.438$
4 O_4	»	»	»	»	$x = 0.267$	$y = 0.383$	$z = 0.425$
4 N	»	»	»	»	$x = 0.250$	$y = 0.038$	$z = 0.058$

The above structural parameters were refined by two least squares calculations, using all 777 observed reflexions of the type $h0l-h3l$. Since the R value did not drop below 24 %, a three-dimensional electron density calculation was performed using the coordinates and isotropic temperature factors from the last shift in the second refinement. This electron density calculation, $\varrho(xyz)$, confirmed the proposed structure except that the y coordinate of O_4 changed from $y=0.39$ to $y=0.05$. Since the picolinate group was expected to be planar, this was quite feasible. Two successive cycles of refinement, in which $|F_o|$ values were scaled separately for each layer, gave $R=17.3$ % and five further cycles with corresponding changes in scale factors and weights gave $R=16.2$ %. The parameters obtained from the last refinement based on the ($h0l-h3l$) data were then used in a refinement based on the ($0kl-5kl$) data (399 reflexions), an R value of 19 % being obtained.

Data from the two series of reflexions were combined by taking a mean value of those structure factors that were in common. This gave 845 independent reflexions which were used in further cycles of refinement.

By assuming the temperature factors to be isotropic the R value dropped to 13.2 % after three cycles of refinement. The final cycles of refinement were calculated allowing for anisotropic temperature factors of all atoms and using a weighting scheme recommended by Cruickshank, $w=(a+|F_o|+c\cdot|F_o|^2+d\cdot|F_o|^3)^{-1}$ with $a=30$, $c=0.02$ and $d=0.0001$. After six cycles of refinement the R value converged to 11.6 % and all parameter shifts were less than 1 % of the standard deviations. A list of observed and calculated structure factors is given in Table 3.

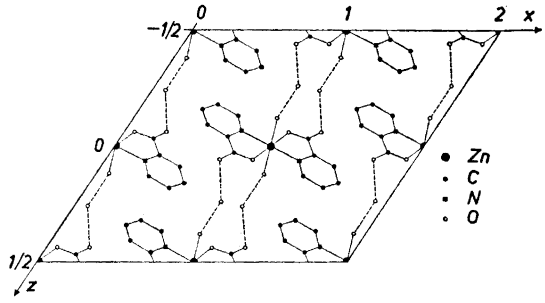

Fig. 4. Projection of the structure on the xz plane. Broken lines denote hydrogen bonds.

Table 3. Calculated and observed structure factors for $Zn(C_6H_4O_2N)_2(H_2O)_4$. Non-observed reflexions are denoted by a dash.

0 0 L		
2	117	97
4	29	33
6	-1	-
8	19	20
10	-8	19
12	22	25
14	17	19
16	34	35
18	18	15
1 0 L		
-18	23	21
-16	36	37
-14	7	-
-12	19	21
-10	34	34
-8	56	64
-6	-31	43
-4	93	95
-2	70	58
0	55	52
2	43	48
4	79	72
6	34	36
8	66	61
10	17	21
12	15	16
14	28	23
16	26	29
2 0 L		
-20	23	22
-18	17	16
-16	21	20
-14	18	20
-12	63	65
-10	47	50
-8	65	64
-6	9	-
-4	-10	24
-2	-13	17
0	66	61
2	-6	14
4	52	52
6	65	60
8	51	55
10	43	41
12	30	32
14	9	-
16	14	12
3 0 L		
-20	16	16
-18	23	24
-16	36	36
-14	24	25
-12	39	44
-10	43	42
-8	44	53
-6	0	-
-4	61	60
-2	64	63
0	67	63
2	56	56
4	34	34
6	44	45
8	34	35
10	-10	22
12	-9	-
14	24	25
4 0 L		
-20	18	-
-18	17	-
-16	24	24
-14	31	35
-12	77	73
-10	69	73
-8	11	9
-6	-13	24
-4	38	41
-2	100	86
0	71	66
2	46	42
4	54	50
6	30	30
8	-15	22
10	6	-
12	14	14

5 0 L		
-22	8	-
-20	24	22
-18	14	-
-16	11	-
-14	43	46
-12	51	50
-10	41	45
-8	27	32
-6	52	55
-4	39	39
-2	16	14
0	-1	10
2	47	53
4	43	46
6	56	50
8	38	34
10	20	21
12	11	-
6 0 L		
-22	33	25
-20	17	19
-18	12	-
-16	1	-
-14	10	-
-12	33	34
-10	57	56
-8	33	35
-6	48	51
-4	20	27
-2	31	38
0	11	-
2	28	32
4	37	38
6	44	42
8	26	28
10	28	22
7 0 L		
-22	13	-
-20	18	-
-18	11	-
-16	12	-
-14	48	55
-12	35	41
-10	43	46
-8	27	32
-6	45	50
-4	40	41
-2	28	33
0	-6	-
2	22	25
4	28	27
6	27	28
8	9	-
8 0 L		
-22	18	-
-20	5	-
-18	16	-
-16	19	24
-14	53	51
-12	59	53
-10	38	41
-8	17	22
-6	45	46
-4	10	25
-2	8	-
0	22	24
2	33	33
4	16	19
6	6	-
9 0 L		
-22	26	-
-20	13	-
-18	8	-
-16	20	21
-14	22	24
-12	-7	-
-10	29	33
-8	48	46
-6	46	40
-4	40	39
-2	29	27
0	10	-
2	15	15
4	14	10
10 0 L		
-20	15	-
-18	13	-

-16	-10	-
-14	1	-
-12	20	21
-10	23	21
-8	38	36
-6	52	47
-4	27	28
-2	18	20
0	17	17
11 0 L		
-20	10	-
-18	14	14
-16	37	34
-14	31	28
-12	7	-
-10	16	18
-8	20	19
-6	18	16
-4	19	16
-2	5	-
12 0 L		
-16	22	16
-14	17	16
-12	15	16
-10	12	-
-8	22	18
0 1 L		
1	79	47
2	35	37
3	35	37
4	11	8
5	36	39
6	39	39
7	48	47
8	26	31
9	26	26
10	-18	20
11	36	37
12	-15	19
13	26	27
14	-4	-
15	20	22
16	2	-
17	11	-
18	5	-
1 1 L		
-19	18	15
-18	7	-
-17	22	21
-16	0	-
-15	18	19
-14	6	-
-13	8	-
-12	20	20
-11	20	18
-10	22	23
-9	42	40
-8	16	17
-7	59	58
-6	-41	44
-5	114	99
-4	-68	57
-3	107	83
-2	-10	8
-1	50	42
0	-43	37
1	-3	9
2	-50	50
3	23	21
4	34	40
5	-9	15
6	32	38
7	34	33
8	3	18
9	34	30
10	-7	18
11	39	33
12	-3	-
13	25	27
14	11	15
15	29	23
16	9	-
17	11	11
2 1 L		
-20	7	-
-19	15	13
-18	1	-
-17	14	12
-16	-4	-

-15	21	20
-14	0	-
-13	36	40
-12	22	22
-11	29	28
-10	17	19
-9	49	50
-8	-31	34
-7	33	37
-6	-5	12
-5	34	33
-4	64	62
-3	16	12
-2	2	8
-1	88	67
0	-38	36
1	33	29
2	-31	38
3	60	58
4	-3	-
5	39	37
6	15	-
7	45	44
8	-9	-
9	22	21
10	-13	10
11	36	33
12	9	-
13	13	-
14	-2	-
15	11	-
16	-12	-
3 1 L		
-20	1	-
-19	9	-
-18	-15	16
-17	21	19
-16	-23	22
-15	16	17
-14	1	-
-13	38	38
-12	19	25
-11	36	32
-10	5	-
-9	50	51
-8	28	30
-7	20	23
-6	37	36
-5	61	60
-4	16	20
-3	2	10
-2	-17	16
-1	44	46
0	-34	38
1	46	38
2	4	9
3	79	73
4	31	33
5	43	44
6	-6	-
7	55	49
8	-8	-
9	16	19
10	-1	-
11	8	-
12	-8	-
13	5	-
14	-7	-
4 1 L		
-21	17	12
-20	-8	-
-19	9	-
-18	-20	21
-17	20	23
-16	-5	-
-15	17	19
-14	5	-
-13	33	36
-12	13	13
-11	23	25
-10	14	14
-9	67	65
-8	2	-
-7	33	34
-6	3	-
-5	61	63
-4	2	-
-3	49	41
-2	-32	33
-1	63	55
0	-16	22
1	13	16
2	-7	15

3	35	34
4	11	12
5	12	16
6	27	27
7	16	19
8	12	17
9	19	17
10	-1	-
11	31	27
12	5	-
13	20	13
5 1 L		
-21	21	18
-20	11	-
-19	28	26
-18	2	-
-17	37	34
-16	-12	-
-15	21	24
-14	-3	-
-13	33	39
-12	1	-
-11	3	-
-10	-20	28
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-5	22	19
-4	7	-
-3	22	19
-2	-1	-
-1	22	19

4 5 L

-15	6	-
-14	3	-
-13	11	-
-12	6	-
-11	9	-
-10	3	-
-9	11	-
-8	6	-
-7	9	-
-6	0	-
-5	17	14

5 5 L

-15	5	-
-14	-1	-
-13	13	-
-12	6	-
-11	14	12
-10	4	-
-9	21	19
-8	8	-
-7	14	-
-6	4	-
-5	19	-
-4	11	-
-3	15	-
-2	-3	-
-1	15	14
0	14	-
1	14	12

0 6 L

0	-7	-
1	5	-
2	4	-
3	4	-
4	18	-

1 6 L

-9	-3	-
-8	8	-
-7	3	-
-6	13	-
-5	1	-
-4	9	-
-3	15	-

2 6 L

-9	-3	-
-8	8	-
-7	1	-
-6	7	-
-5	2	-
-4	18	-
-3	-1	-

3 6 L

-10	7	-
-9	-3	-
-8	12	-
-7	-5	-
-6	17	13
-5	-5	-
-4	13	14

Table 4. Atomic coordinates, expressed in fractions of the cell edges, with anisotropic temperature factors.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0	0	0	0.0027	0.0228	0.00164	0.0015	0.0025	0.0026
C_1	0.4923	0.128	0.0871	0.0041	0.038	0.0024	0.002	0.0036	−0.001
C_2	0.3259	0.104	0.0433	0.0040	0.011	0.0024	0.005	0.0042	0.006
C_3	0.2104	0.211	0.4692	0.0023	0.023	0.0015	−0.003	−0.0008	0.000
C_4	0.4068	0.444	0.3433	0.0062	0.014	0.0029	−0.001	0.0041	−0.003
C_5	0.3485	0.762	0.1298	0.0043	0.026	0.0025	0.000	0.0042	−0.001
C_6	0.4831	0.261	0.3236	0.0041	0.025	0.0026	−0.011	0.0040	−0.006
O_1	0.0727	0.980	0.2565	0.0148	0.035	0.0027	0.005	0.0061	0.002
O_2	0.0792	0.244	0.1190	0.0069	0.027	0.0011	0.004	0.0040	0.001
O_3	0.0612	0.218	0.4401	0.0027	0.023	0.0021	−0.003	0.0034	−0.004
O_4	0.2713	0.067	0.4396	0.0070	0.030	0.0032	0.004	0.0062	−0.008
N	0.2533	0.917	0.0652	0.0023	0.015	0.0005	0.010	−0.0001	0.002

Table 5. Standard deviations of the atomic parameters.

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(\beta_{11})$;	$\sigma(\beta_{22})$	$\sigma(\beta_{33})$	$\sigma(\beta_{12})$	$\sigma(\beta_{13})$	$\sigma(\beta_{23})$
Zn	—	—	—	0.0003	0.0012	0.00010	0.0012	0.0003	0.0007
C_1	0.0016	0.004	0.0010	0.0019	0.008	0.0007	0.006	0.0020	0.004
C_2	0.0015	0.003	0.0010	0.0017	0.006	0.0006	0.005	0.0018	0.003
C_3	0.0015	0.003	0.0009	0.0016	0.008	0.0006	0.006	0.0016	0.003
C_4	0.0017	0.003	0.0010	0.0019	0.009	0.0007	0.006	0.0020	0.003
C_5	0.0016	0.003	0.0010	0.0019	0.008	0.0007	0.006	0.0019	0.004
C_6	0.0016	0.003	0.0010	0.0018	0.008	0.0007	0.006	0.0019	0.004
O_1	0.0015	0.003	0.0007	0.0020	0.006	0.0005	0.007	0.0017	0.004
O_2	0.0012	0.002	0.0006	0.0015	0.005	0.0004	0.004	0.0013	0.002
O_3	0.0010	0.002	0.0006	0.0013	0.005	0.0004	0.004	0.0013	0.002
O_4	0.0012	0.002	0.0007	0.0015	0.007	0.0005	0.004	0.0015	0.003
N	0.0012	0.002	0.0007	0.0013	0.006	0.0004	0.004	0.0013	0.002

Table 6. Distances and angles in the zinc picolinate molecule.

$Zn-O_2$	2.18 ± 0.01 Å	C_2-N	1.38 ± 0.02 Å
$Zn-O_3$	2.08 ± 0.01 Å	C_3-C_2	1.50 ± 0.02 Å
$Zn-N$	2.10 ± 0.01 Å	C_3-O_3	1.24 ± 0.02 Å
C_1-C_2	1.36 ± 0.02 Å	C_3-O_4	1.23 ± 0.02 Å
C_1-C_4	1.42 ± 0.02 Å	O_2-O_3	2.73 ± 0.02 Å
C_4-C_6	1.37 ± 0.02 Å	O_2-O_1	2.80 ± 0.02 Å
C_5-C_6	1.36 ± 0.02 Å	O_1-O_4'	2.69 ± 0.02 Å
C_5-N	1.27 ± 0.02 Å	O_2-O_3'	2.73 ± 0.02 Å
$Zn-N-C_2$	109.3 ± 0.8°	$C_2-C_1-C_4$	117.0 ± 1.1°
$Zn-N-C_5$	131.6 ± 0.9°	C_1-C_2-N	123.1 ± 1.2°
O_2-Zn-O_3	89.1 ± 0.4°	$C_1-C_2-C_3$	120.6 ± 1.2°
C_2-N-C_5	117.6 ± 1.1°	$C_2-C_3-O_3$	118.4 ± 1.3°
$N-C_5-C_6$	124.8 ± 1.4°	$C_2-C_3-O_4$	116.8 ± 1.1°
$C_5-C_6-C_4$	119.2 ± 1.5°	$O_4-C_3-O_3$	124.8 ± 1.4°
$C_6-C_4-C_1$	118.3 ± 1.2°		

The resulting parameters and the corresponding standard deviations are given in Tables 4 and 5. The interatomic distances and angles were calculated on the basis of the coordinates in Table 4 (*cf.* Table 6). Fig. 4 shows the projection of the structure on the *xz* plane. The picolinate group and the arrangement of ligands around the zinc atom are shown in Figs. 5 and 6, respectively.

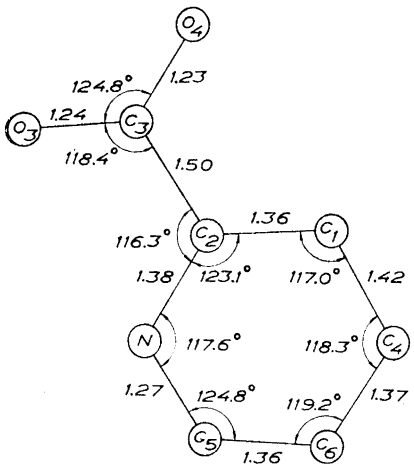

Fig. 5. Schematic drawing of the picolinate group.

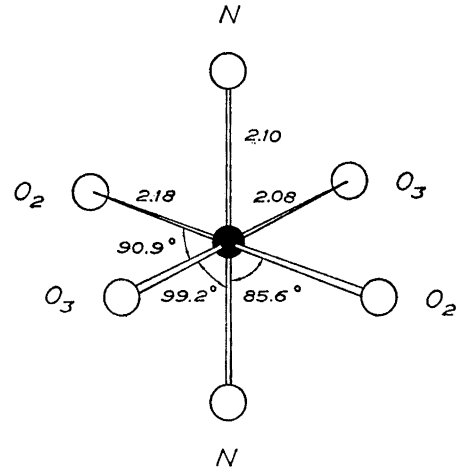

Fig. 6. Schematic representation of the octahedral configuration about the central zinc atom.

DISCUSSION OF THE STRUCTURE

The $Zn(C_6H_4O_2N)_2(H_2O)_4$ molecule is centrosymmetric, the zinc atom being octahedrally coordinated by two nitrogen and four oxygen atoms, two of which, O_3, belong to carboxylate groups. That the picolinate ligands are bonded to zinc through the carboxylate groups is also apparent from a comparison of the infrared spectra of picolinic acid and zinc picolinate, since the band due to CO stretching in the region 1600 cm^{-1} is much stronger for zinc picolinate than for the free acid.

The $Zn-O_3$ bond distance is 2.08 Å which is within the normal range but the distances between zinc and the coordinated water molecules ($Zn-O_2$) are somewhat longer (2.18 Å). The structure contains two further water molecules situated between two adjacent zinc picolinate groups, the O_2-O_1 and O_1-O_4' distances being 2.80 Å and 2.69 Å, respectively, where O_4' belongs to the nearest neighbouring molecule. The long $Zn-O_2$ distance can thus be explained by hydrogen bonding.

This structure determination was completed at the beginning of 1968. Quite recently, however, we became aware that preliminary structure details of the corresponding nickel compound has been published by Loiseleur, Thomas, Chevrier and Grandjean.[8] As far as it is possible to judge from their paper the structural features of the two compounds seem to be similar.

Zn^{2+} has a complete 18 electron shell, and though zinc complexes are often 4-coordinated by a tetrahedral arrangement of ligands, the electronic structure of Zn^{2+} makes the formation of 6-coordinated complexes possible. The transformation of electronic configuration for Zn from $d^{10}s^2$ to $d^9s^2p^1$ involves an energy of $\simeq 560$ kJ/mole, the corresponding wavelength being 2138 Å.[9] This energy is of a magnitude that makes it quite possible for the d electrons to contribute to the bonding of the ligands. The d electron configuration for Zn is, according to ligand field theory, $(t_{2g})^6(e_g)^4$. Thus together with the 12 electrons available for bonding in the ligands, the resulting molecular electronic configuration for the zinc complex is $(a_{1g}{}^b)^2(t_{1u}{}^b)^6(e_g{}^b)^4(t_{2g})^6(e_g{}^*)^4$. Owing to the filled antibonding orbitals $(e_g{}^*)^4$, the bonds in the 6-coordinated zinc complex ought to be weaker than those in a 4-coordinated complex. As expected, the six bond lengths have a mean value of 2.15 Å (*cf.* Table 6) which is somewhat longer than the average 4-coordinated Zn—O bond distance (1.97 Å) in zinc oxyacetate, $Zn_4O(CH_3COO)_6$.[7] Other zinc complexes containing carboxylate groups in which zinc has been found to be octahedrally coordinated are $Zn(ADA)_2$,† $Zn(ATA)_2$,† Zn(EDTA) [10] and $Zn(CH_3COO)_2(H_2O)_2$.[11] That the octahedral configuration about zinc in zinc picolinate is somewhat distorted can probably be explained in terms of a π-bonding contribution.

The zinc atom in 0,1/2,1/2 and its four coordinated oxygen atoms lie in one plane owing to the symmetry of the space group. The equation of this plane is $-0.8054X-0.3739Y-0.4598Z=-0.3711$, where X, Y, and Z are expressed in Ångströms. The angles O_2—Zn—N and O_3—Zn—N are $85.6° \pm 0.4$ and $80.0° \pm 0.4$, respectively. According to least squares calculations the best fitting plane through the carbon and the nitrogen atoms of the picolinate group associated with Zn at 0,1/2,1/2 has the equation $0.4076X+0.6048Y-$ $-0.6842Z=-4.9987$. The angle between the zinc-oxygen plane and the picolinate plane is 103.9°.

Owing the resonance in the carboxylate groups of the molecule, the C—O distances are identical within the limits of experimental error (*cf.* Table 6). The two oxygen atoms of the carboxylate group lie 0.19 Å above (O_4) and 0.17 Å below (O_3) the least squares plane for the picolinate group. The angle between the plane of the picolinate group and that of the carboxylate group is thus 9.6°.

As seen from Fig. 4, the structure can be described as consisting of rows of parallel molecules held together by hydrogen bonding along the z axis via water molecules. In the y direction there ought to be hydrogen bonds between adjacent molecules, since the distance between an O_2 atom and an O_3 atom of the neighbouring molecule is 2.73 Å. The picolinate groups of two neighbouring molecules make an angle of 74° with one another. The shortest v.d. Waals distance between the molecules is $\simeq 4.6$ Å.

The authors wish to thank Dr. Dennis B. McWhan, Bell Telephone Laboratory, for help with the preliminary computer calculations and Dr. Nils-Gösta Vannerberg of this Department for valuable discussions on the theoretical aspects connected with this structure. Many thanks are also due to Mrs. Susan Jagner, M.A., fil.lic. for revising the English text of this paper.

† ADA = Ammonium diacetate, $HN(CH_2COO)_2^{2-}$
ATA = Ammonium triacetate, $N(CH_2COO)_3^{3-}$.

Financial support has been provided by the *Swedish Natural Science Research Council* (Contract No. 2318) and the costs of the computer work, performed at *Gothenburg Universities' Computing Center* (SAAB D21 and IBM 360/50), have been covered by a grant from *Chalmers University of Technology*. One of us, Paavo Lumme, would also like to express his thanks to the *National Research Council for Science (Finland)* for financial support.

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Received March 28, 1969.