The OD-groupoid family is

$$P(1)\frac{2}{c}1\;[.\tfrac{1}{4}.]\;A(1)\frac{2}{m}1\,.$$

The structure contains two kinds of large ordered domains with space group $I1\frac{2}{c}1$ and $P1\frac{2}{c}1$ corresponding to the strong maxima and the weak maxima respectively. Based on the OD theory, methods have been developed to determine the structures of the two kinds of layers (Figs. 5 and 6). The *A* layers (each of them contains only one O atom in the asymmetric unit) with the higher symmetry lie ordered (periodic vector **a**/2). The *P* layers may occupy either of two equivalent positions characterized by the vectors between the mirror planes of the *A* layers and the *c* glides of the adjacent *P* layers $(.\tfrac{1}{4}.)$.

The structures of domains MDO(1) and MDO(2) (Figs. 5 and 6) have been determined independently, one from the other, using sharp reflexions and strong maxima, or sharp reflexions and weak maxima, respectively. For both kinds of domains the result of the structure determination is practically the same in agreement with our assumption (Table 3).

The results of this paper show, that apparently different modifications of calcium monoborate dihydrate described by Kravchenko (1964), Ozol, Wimba & Jevinsh (1964) and by Sedlacek (1966) and such modifications which were assumed by mistake to be calcium diborate hexahydrate, described by Peacock & Vigfusson (1939) and Ghose (1963) belong to the same OD-structure family as described in this paper.

The different modifications are either members of this family with maximum degree of order (those described by Kravchenko and Ozol *et al.*) or one-dimensionally disordered members with different degrees of disorder (those described by the other authors quoted above). The structure determined by Kravchenko is in very good agreement with the structure of domains MDO(1) and that determined by Ozol *et al.* is obviously the same as MDO(2) (Table 3). Only the interpretation of the O–H–O bonds is rather different (§ 6).

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The Crystal and Molecular Structure of Ethylenebisbiguanidenickel(II) Chloride Monohydrate, $C_6H_{16}N_{10}NiCl_2.H_2O$

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(*Received* 1 *May* 1970)

Ethylenebisbiguanidenickel(II) chloride monohydrate, $C_6H_{16}N_{10}Ni.Cl_2H_2O$, crystallizes in the monoclinic system with $a=6{\cdot}905\ (5)$, $b=11{\cdot}680\ (4)$, $c=18{\cdot}038\ (23)$ Å, $\beta=101{\cdot}41\ (10)^\circ$, $D_m=1{\cdot}740$ g.cm^{-3}, $Z=4$, $D_x=1{\cdot}750$ g.cm^{-3}; the space group is $P2_1/c$. The structure was determined by using 1714 'observed' intensities collected on a General Electric XRD-5 diffractometer using Mo $K\alpha$ radiation and the parameters were refined by least-squares until $R=0{\cdot}031$. The nickel atom is in square planar configuration with an average Ni–N bond length of 1·866 Å. The tetradentate ethylenebisbiguanide ligand is essentially planar around the nickel. Through extensive hydrogen bonding involving the water of hydration and the two chloride ions, the molecules are formed into infinite sheets parallel to the (100) planes. Additional hydrogen bonds between the sheets create a rigidly bound structure. A particularly interesting feature of the hydrogen bonding is the discovery of five bonds involving the water of hydration. This report presents the third independent solution and refinement of the structure. A comparison with the structure reported by Holian & Marsh using the δ_p half-normal probability plot, indicates that most of the standard deviations derived in both studies are too small by a factor of about 1·7; some are too small by a considerably larger factor.

Introduction

The X-ray crystal structure study of ethylenebisbiguanidenickel(II) chloride monohydrate was undertaken owing to the interest in multidentate ligands and interest in organic compounds of transition metals. The present compound combines these qualities and is of special interest because of the tetradentate nature of the ethylenebisbiguanide ligand.

After this study was completed, it was discovered

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* Petroleum Research Fund Fellow 2022A3.

that this crystal structure had been examined by Holian & Marsh (1970) and by Coghi, Mangia, Nardelli & Pelizzi (1969). The accuracy of the two sets of diffractometer data (Holian & Marsh's and the present authors') collected and interpreted independently in two different laboratories using different radiations, makes for an interesting and worthwhile comparison of the final structures.

Experimental

Preliminary photographic examination of a single crystal of ethylenebisbiguanidenickel(II) chloride monohydrate,* $C_6H_{16}N_{10}NiCl_2 . H_2O$, showed the conditions for reflection to be $h0l$: $h+l=2n$, and $0k0$: $k=2n$, uniquely determining the space group $P2_1/n$.† Precise unit-cell parameters were determined on a General Electric XRD-5 diffractometer and single crystal orienter using Mo $K\alpha$ radiation by least-squares refinement of 14 2θ values. The crystal data are listed in Table 1.

Table 1. *Crystal data*

Ethylenebisbiguanidenickel(II) chloride monohydrate
$C_6H_{16}N_{10}NiCl_2.H_2O$ F.W. 375·91 $F(000)=776$

Monoclinic, space group $P2_1/c$
$a=$ 6·905 (5) Å
$b=11·680$ (4)
$c=18·038$ (23)
$\beta=101·41$ (10)°
$V=1426·0$ Å^3 $D_m=1·740$ g.cm^{-3}
$Z=4$ $D_x=1·750$ g.cm^{-3}

The presence of one molecule of water per formula unit was determined from the weight loss of a finely ground sample heated to 110°C for 16 hours; a loss of 4·86% was observed compared with a theoretical loss of 4·79%. The density, measured by flotation in a bromoform–carbon tetrachloride mixture is 1·740 g.cm^{-3}. For $Z=4$, the calculated density is 1·750 g.cm^{-3}.

The unique intensity data were collected by θ–2θ scans using zirconium-filtered Mo $K\alpha$ radiation ($\lambda=0·7107$ Å) and a General Electric XRD-5 diffractometer equipped with a scintillation counter, pulse-height discriminator, and a General Electric single crystal orienter. The crystal was mounted with the a axis parallel to the spindle axis. Sixty-second scans (2° in 2θ) were used with stationary backgrounds measured for 30 seconds each at the start and finish of each scan. A chart recording of diffracted intensity *vs.* 2θ was monitored during data collection to ensure that the reflections were centered in the scan range. The intensities of the standard reflections monitored during data collection showed no systematic variations; there was no evidence of radiation damage to the crystal. Of the 2228 unique reflections which were examined within the range $2\theta \le 48°$, 1714 had an intensity greater than twice the standard deviation of the intensity; the remaining 514 reflections were coded as 'unobserved' and were not included in the refinement.

The individual R values for the six most intense reflections are considerably larger than the overall R value indicating possible coincidence loss errors although there is no pattern in the individual R values. These reflections, each with the scan peak counts $\times 10^{-4}$ and the individual R values, are: $20\bar{2}$, 196, 11·1%; 011, 196, 7·0%; 002, 155, 0·9%; 200, 130, 27·5%; 033, 88, 4·3%; and $21\bar{2}$, 84, 0·2%. These data are included in the final refinement.

The dimensions of the crystal were measured, in preparation for applying absorption corrections, using a calibrated 'Whipple disc' in the alignment telescope.*

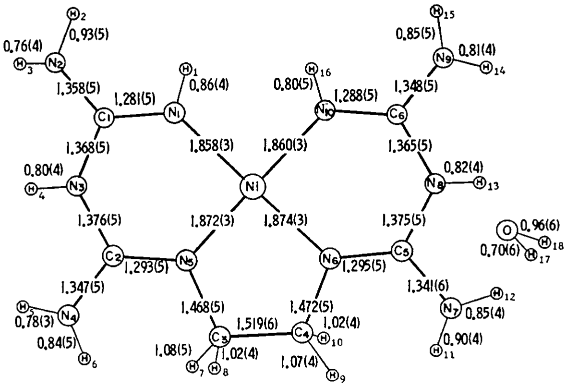

Fig. 1. Bond lengths of the ethylenebisbiguanidenickel(II) complex ion and the water of hydration.

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* The crystals used in this investigation were supplied by Dr David J. MacDonald, Department of Chemistry, University of Nevada, Reno, Nevada, U.S.A. 89507. The preparation of the compound is described by MacDonald (1967).

† The $P2_1/n$ cell was used throughout this study of the structure. It is the 'best' choice of cell for this crystal in that $\beta=100·68°$ for $P2_1/n$ while $\beta=101·41°$ for $P2_1/c$. In the interest of accepting the setting of the first publications of the structure (Coghi *et al.*, 1969; Holian & Marsh, 1970) and for making it less difficult to compare the results of this study with those of Holian & Marsh, all data and results have been transformed into the $P2_1/c$ cell and the numbering of the atoms has been changed to be consistent with Holian & Marsh.

The transformation matrices are:

$$(hkl)\times\begin{vmatrix} 1 & 0 & -1 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}=(h'k'l')$$

$$(xyz)\times\begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ -1 & 0 & -1 \end{vmatrix}=(x'y'z')$$

$$(\beta_{11}\beta_{22}\beta_{33}\beta_{12}\beta_{13}\beta_{23})\times\begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ -2 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{vmatrix}=(\beta_{11}'\beta_{22}'\beta_{33}'\beta_{12}'\beta_{13}'\beta_{23}')$$

where the unprimed parameters refer to $P2_1/n$ and the primed (′) refer to $P2_1/c$ and where the β_{ij} are in the usual matrix form, *i.e.* the term in the exponential of the temperature factor is

$$\sum_{i=1}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}.$$

* See Ward & Caughlan (1971) for details of the measurement procedure.

The crystal was well-shaped, bound by the planes $\{10\bar{1}\}$, $\{001\}$, $\{011\}$, and $\{01\bar{1}\}$, and its dimensions in the directions of a, b, and c^* were approximately 0·82 mm, 0·28 mm, and 0·13 mm, respectively. The linear absorption coefficient for Mo $K\alpha$ radiation is 18·21 cm^{-1}; absorption corrections were applied using the method of de Meulenaer & Tompa (1965) calculating transmission coefficients (I/I_0) ranging from 0·895 to 0·763.

Structure determination and refinement

All calculations were carried out on an XDS Sigma 7 computer.* Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for all atoms other than hydrogen; those for hydrogen

Table 2. *Observed and calculated structure factors*

H= 0	K= 0	
L	FO	FC
2	145	146
4	65	65
6	120	118
8	187	183
10	95	92
12	36	37
14	60	59
16	17	19
18	23	23
20	17	18
H= 0	K= 1	
L	FO	FC
-1	129	138
-2	50	49
-3	79	77
-4	8	9
-5	79	77
-6	35	35
-7	18	20
-8	24	22
-9	121	117
-11	40	38
-12	23	23
-13	18	17
-14	10	10
-15	18	16
-16	14	15
-17	18	18
H= 0	K= 2	
L	FO	FC
0	60	59
-1	6	3
-3	30	31
-4	30	32
-5	42	42
-6	103	101
-7	11	12
-8	52	51
-9	13	13
-11	7	7
-12	38	38
-13	12	11
-14	34	34
-15	10	10
-16	21	23
-17	23	23
-18	13	15
-20	20	21
H= 0	K= 3	
L	FO	FC
-2	6	8
-3	169	176
-4	21	21
-5	15	13
-6	25	24
-7	57	55
-9	30	30
-10	21	21
-11	84	82
-12	53	53
-13	6	5
-14	15	15
-15	25	27
-16	16	17
-17	27	27
-18	30	30
H= 0	K= 4	
L	FO	FC
0	24	23
-1	17	18
-2	88	86
-3	16	15
-4	41	42
-6	37	36
-7	16	17
-8	28	26
-9	27	26
-10	26	25
-11	31	29
-12	53	52
-13	36	35
-15	22	21
-19	21	21
H= 0	K= 5	
L	FO	FC
-1	19	17
-2	16	15
-3	78	76
-4	39	37
-6	48	48
-8	15	14
-9	36	36
-10	72	70
-11	51	50
-12	38	38
-13	24	24
-14	26	26
-15	14	15
-16	9	9
-17	7	7
-18	37	38
H= 0	K= 6	
L	FO	FC
0	24	23
-1	50	50
-2	8	9
-3	17	18
-4	30	29
-5	25	24
-7	35	35
-8	7	6
-9	51	49
-12	23	22
-13	13	14
-14	22	21
-15	57	56
-16	19	20
-17	8	9
H= 0	K= 7	
L	FO	FC
-1	10	11
-2	5	4
-3	7	7
-4	26	25
-5	5	6
-6	26	24
-7	36	34
-9	7	7
-10	29	29
-11	20	20
-12	12	11
-14	12	17
-15	13	13
-16	17	17
H= 0	K= 8	
L	FO	FC
0	19	19
-1	7	7
-2	47	46
-3	35	35
-4	8	8
-5	15	15
-6	30	29
-7	37	36
-8	25	25
-9	39	40
-10	16	16
-12	10	10
-13	34	34
-14	12	12
-15	30	30
-16	12	11
H= 0	K= 9	
L	FO	FC
-1	23	23
-2	31	30
-3	42	40
-5	35	34
-6	10	11
-7	29	29
-8	28	28
-9	22	21
-11	23	24
-12	45	45
-13	19	20
H= 0	K= 10	
L	FO	FC
-1	10	9
-4	26	25
-5	21	19
-6	17	17
-7	33	34
-8	18	16
-9	12	11
-11	8	9
-12	8	9
H= 0	K= 11	
L	FO	FC
-2	18	18
-3	42	41
-5	51	51
-6	22	21
-8	15	15
-9	26	24
-11	15	14
H= 0	K= 12	
L	FO	FC
0	52	52
-1	30	29
-2	32	32
-6	35	35
-8	27	27
H= 0	K= 13	
L	FO	FC
-1	28	28
-3	36	35
H= 1	K= 0	
L	FO	FC
0	38	37
2	8	7
-2	33	34
4	29	30
-4	37	37
6	102	101
-6	65	63
8	69	66
-8	45	45
10	56	54
-10	89	89
-12	25	24
14	68	66
-14	58	59
-16	26	25
-20	25	27
H= 1	K= 1	
L	FO	FC
0	14	12
1	33	35
-1	4	4
2	56	57
-2	68	69
3	28	28
-3	42	43
4	32	33
-4	30	31
5	62	65
-5	104	105
6	16	14
-6	42	42
8	36	37
-8	37	35
9	45	47
-9	24	22
-10	38	38
11	41	44
-11	64	64
12	9	9
-12	15	17
13	7	6
-13	29	29
14	11	10
15	14	12
16	10	8
17	26	26
-17	12	13
19	33	33
-19	49	50
-20	14	16
H= 1	K= 2	
L	FO	FC
0	8	7
1	23	22
-1	50	50
2	28	28
3	13	12
4	23	22
-4	6	6
-5	43	44
6	37	35
-6	22	23
7	102	99
-7	97	97
8	56	54
-8	75	73
9	15	15
-9	9	7
-10	16	15
11	36	34
-11	18	19
12	44	43
13	19	19
14	48	47
-14	33	33
15	18	16
-15	19	18
16	22	22
-16	28	28
18	16	16
-18	14	15
19	12	12
-19	11	14
-20	21	21
H= 1	K= 3	
L	FO	FC
0	24	27
1	54	55
-1	63	66
2	145	145
-2	61	61
3	87	88
-3	52	52
4	35	33
-4	78	78
5	9	9
-5	43	42
6	45	43
-6	76	75
7	19	17
-7	41	40
8	43	42
-8	37	35
9	27	27
10	55	54
-10	33	33
11	69	67
-11	46	45
12	41	40
-12	58	59
13	32	32
-13	61	62
14	22	22
-14	27	27
15	6	5
16	37	36
-16	34	34
17	54	54
-17	43	44
-18	16	18
19	14	15
-19	25	25
-20	13	14
H= 1	K= 4	
L	FO	FC
0	24	23
1	70	68
-1	99	99
-2	26	26
3	28	28
4	34	33
-4	19	19
5	26	26
6	10	11
-6	19	21
7	52	50
-7	60	60
8	57	55
-8	79	77
9	27	26
-9	54	53
10	10	9
11	28	27
-11	41	41
12	12	10
-12	19	18
13	22	22
-13	57	58
-15	21	22
16	21	21
-16	44	45
17	8	8
-17	16	17
-18	9	9
-19	19	18
H= 1	K= 5	
L	FO	FC
0	104	102
1	23	23
-1	27	27
2	80	77
-2	44	42
3	45	42
-3	77	76
4	86	85
-4	125	125
-5	72	69
6	6	5
-6	25	24
7	7	8
-7	9	9
8	59	58
-8	28	28
9	10	10
-9	16	16
10	73	71
-10	73	72
11	6	6
-12	40	39
13	40	40
-13	37	38
14	13	12
-14	16	13
-15	19	19
16	12	12
17	23	23
-17	17	17
18	19	19
-18	26	26
H= 1	K= 6	
L	FO	FC
1	94	91
-1	134	135
-2	35	35
3	41	39
-3	19	18
4	62	60
-4	50	48
5	123	121
-5	69	69
6	15	14
-6	9	7
7	56	55
-7	56	56
8	15	14
-8	20	19
9	60	59
-9	74	74
-10	30	30
11	18	18
12	42	41
-12	31	31
13	57	56
-13	29	29
-14	9	9
15	9	10
-15	14	14
16	9	9
-16	12	12
17	17	17
-17	10	12
H= 1	K= 7	
L	FO	FC
0	40	38
1	18	18
-1	22	20
2	57	56
-2	30	30
-3	19	20
4	86	85
-4	75	76
5	25	23
6	19	18
-6	43	42
8	37	37
-8	25	24
9	11	10
-9	13	13
10	33	31
-10	45	45
11	12	14
-11	8	7
-12	7	5
14	19	19
15	9	9
-15	14	14
16	16	16
-16	24	24
H= 1	K= 8	
L	FO	FC
1	58	57
-1	95	94
2	12	12
-2	13	13
3	34	34
-3	60	60
5	55	55
-5	34	33
6	12	12
-6	9	9
7	66	65
-7	77	76
-8	13	12
-9	27	26
10	8	7
11	31	31
-11	31	32
-12	23	23
13	22	22
-13	30	30
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-14	8	8
15	10	11
-15	30	31
-16	17	17
H= 1	K= 9	
L	FO	FC
1	43	43
2	77	75
-2	64	63
3	23	23
-3	18	18
4	24	23
-4	50	49
-5	11	11
6	25	25
-6	29	29
-7	9	10
8	27	28
-8	12	13
9	11	12
-9	7	8
10	38	38
-10	38	38
11	25	26
-11	18	19
12	17	17
-12	34	35
13	10	10
-13	13	13
14	9	8
-15	15	14
H= 1	K= 10	
L	FO	FC
0	7	7
1	11	10
-1	12	12
2	32	32
-2	23	22
3	9	8
-3	9	9
5	11	10
6	9	8
-6	6	6
7	23	23
-7	35	35
9	11	10
10	19	19
-10	17	17
11	28	27
-11	12	12
12	10	12
-13	20	20
H= 1	K= 11	
L	FO	FC
1	8	7
-1	19	18
2	23	23
-3	6	6
4	18	18
-4	27	28
5	18	18
-5	24	25
-6	8	9
-7	7	8
8	15	13
-8	9	10
9	12	11
-9	12	12
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-10	24	24
-11	14	13
H= 1	K= 12	
L	FO	FC
1	10	10
-1	17	17
2	8	6
3	8	7
-3	8	7
5	20	20
-5	11	12
6	17	18
-6	10	11
7	7	6
-7	9	9
-8	13	14
-9	9	9
H= 1	K= 13	
L	FO	FC
1	8	7
-2	11	11
3	10	9
-4	12	11
H= 2	K= 0	
L	FO	FC
0	282	359
2	39	42
-2	229	254
4	110	111
-4	55	53
6	105	104
-6	30	28
8	111	108
-8	96	96
10	45	45
-10	96	96
12	38	38
-12	29	29
14	27	26
-14	53	54
16	14	13
18	28	28
-18	9	7
-20	17	19
H= 2	K= 1	
L	FO	FC
0	165	178
1	149	151
-1	131	135
2	45	45
-2	65	65
3	73	71
-3	41	37
4	33	32
-4	19	19
5	24	22
-5	108	108
6	10	11
-6	39	39
7	48	44
-7	17	14
8	46	45
-8	35	34
9	116	116
-9	72	71
10	17	18
-10	58	58
11	6	7
-11	58	57
12	15	15
-12	22	23
13	21	22
-13	30	30
-14	18	19
15	20	20
-15	11	11
16	8	7
-16	18	20
17	8	8
-17	28	29
-18	10	10
-19	11	12
-20	8	8
H= 2	K= 2	
L	FO	FC
0	73	73
-1	37	39
2	27	25
-2	69	68
3	10	11
-3	95	98
4	40	39
5	34	34
-5	42	42
6	76	75
-6	37	36
-7	21	21
8	9	8
-8	92	92
10	22	22
-10	26	28
-11	25	26
12	40	40
-12	30	31
13	17	16
-13	8	10
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6	10	10
8	18	18
-8	22	22
-10	21	22
-12	24	24
-14	13	14
-16	13	13
H= 6	K= 1	
L	FO	FC
0	9	8
1	35	35
-1	48	48
2	8	7
-2	28	27
3	16	16
-3	38	39
4	9	9
5	34	33
-5	33	33
-6	12	13
7	30	29
-7	22	22
8	14	14
-8	9	8
9	21	21
-9	30	29
-10	11	11
-11	28	28
-12	9	8
-13	37	38
H= 6	K= 2	
L	FO	FC
0	38	38
-1	48	47
2	30	30
-2	56	55
3	13	12
4	25	26
-4	42	42
6	20	22
-6	25	27
7	19	19
8	27	27
-8	23	24
9	9	9
-9	13	13
-10	38	37
-12	31	32
-13	21	20
-14	24	24
-15	8	6
H= 6	K= 3	
L	FO	FC
0	18	17
1	21	22
-1	38	37
2	8	7
-3	21	20
4	7	6
-4	16	16
-5	20	20
7	22	23
-7	35	36
8	16	16
-9	16	15
-11	34	33
-12	24	22
-13	24	24
-14	19	18
-15	28	27
H= 6	K= 4	
L	FO	FC
1	11	11
2	24	22
-2	25	25
-3	9	8
-4	12	11
5	11	10
-5	15	15
-6	23	23
-10	26	25
-11	21	20
-12	13	13
-13	14	14
H= 6	K= 5	
L	FO	FC
1	12	12
-1	7	7
2	16	16
-3	9	9
-4	14	14
6	17	17
-7	11	11
-10	13	13
-12	8	7
H= 6	K= 6	
L	FO	FC
1	14	15
-3	18	17
-4	13	13
5	18	19
-5	12	12
-11	9	9
H= 6	K= 7	
L	FO	FC
2	16	16
-3	11	11
4	10	11
-4	11	11
-7	10	8
-8	11	11
-10	8	6
H= 6	K= 8	
L	FO	FC
1	8	7
-2	8	8
-6	14	13
H= 7	K= 0	
L	FO	FC
2	9	9
-2	11	9
4	8	9
-6	14	13
-8	12	11
-10	12	11
H= 7	K= 1	
L	FO	FC
1	17	17
2	15	15
-2	9	8
-3	8	7
5	13	14
-6	7	7
-9	10	10
-12	8	8
H= 7	K= 2	
L	FO	FC
1	16	16
-1	14	13
-2	7	4
3	14	11
-3	18	18
4	9	9
-5	13	14
-7	19	19
-10	8	8
-11	23	23
-12	16	15
H= 7	K= 3	
L	FO	FC
-1	8	7
2	9	10
-2	24	23
3	8	8
-4	15	15
-5	22	21
-6	28	27
-8	16	16
-9	10	9
-10	16	16
H= 7	K= 4	
L	FO	FC
1	16	16
-1	17	18
-2	12	11
3	12	11
-3	13	13
-5	17	23
-6	11	10
-7	22	22
-8	8	7
-9	22	22
H= 7	K= 5	
L	FO	FC
0	29	29
-2	17	16
-4	20	20
-6	16	16
-7	10	10
-8	27	27
-9	11	10

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* Computer programs used were by F. R. Ahmed and coworkers (NRC-2, Data Reduction and Tape Generation; NRC-8, Fourier for Distorted and Undistorted Nets; NRC-10, Structure Factor Least Squares (Block Diagonal); and NRC-12, Scan of Interatomic Distances and Angles, National Research Council, Ottawa, Ontario, Canada) and Busing & Levy (1959). These programs were locally modified for use with the XDS Sigma 7 computer. Other programs were written locally by C. N. Caughlan, E. L. Enwall, G. D. Smith, D. L. Ward, and K. D. Watenpaugh.

Table 3. *Parameters of non-hydrogen atoms and their estimated standard deviations*

The expression for the anisotropic temperature factors is in the form
$\exp\,[-(\beta_{11}h^2-\beta_{22}k^2-\beta_{33}l^2-\beta_{12}hk-\beta_{13}hl-\beta_{23}kl)]$

	Positional parameters × 10^5			Thermal parameters × 10^5					
	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	25732 (8)	3911 (5)	884 (3)	1382 (13)	364 (4)	155 (2)	10 (14)	204 (8)	−14 (4)
Cl(1)	24722 (20)	−36131 (10)	−27530 (7)	2544 (38)	608 (11)	288 (5)	−86 (32)	322 (22)	−228 (12)
Cl(2)	33294 (23)	−2866 (11)	−34622 (7)	4175 (49)	570 (11)	229 (5)	−448 (38)	280 (24)	106 (12)
O	12338 (61)	−44841 (34)	−12580 (20)	3880 (134)	1256 (44)	325 (15)	−800 (124)	652 (70)	−290 (44)
N(1)	28924 (54)	7859 (28)	11031 (19)	2143 (109)	404 (29)	167 (13)	−34 (88)	310 (60)	16 (30)
N(2)	36003 (59)	19295 (32)	21832 (20)	2826 (130)	654 (37)	164 (14)	−370 (108)	272 (68)	−76 (36)
N(3)	36336 (56)	27037 (29)	10203 (19)	2363 (116)	382 (30)	193 (14)	−300 (92)	192 (62)	−88 (32)
N(4)	34903 (61)	38741 (30)	51 (19)	3366 (135)	417 (31)	184 (14)	−324 (106)	394 (70)	−58 (32)
N(5)	29596 (50)	19055 (28)	−1901 (18)	1716 (105)	389 (30)	183 (13)	−26 (84)	226 (58)	−20 (30)
N(6)	22583 (51)	377 (27)	−9417 (19)	1741 (103)	411 (29)	158 (12)	92 (82)	214 (56)	−56 (30)
N(7)	17480 (64)	−11330 (32)	−20065 (21)	3271 (138)	546 (34)	206 (15)	6 (108)	410 (72)	−148 (36)
N(8)	16406 (55)	−19202 (28)	−8617 (19)	2333 (115)	358 (30)	207 (14)	−28 (92)	294 (64)	−104 (32)
N(9)	15385 (62)	−30725 (30)	1507 (22)	2943 (131)	406 (32)	289 (16)	−174 (106)	258 (72)	72 (36)
N(10)	21747 (54)	−11245 (29)	3347 (20)	2075 (109)	408 (30)	205 (14)	−16 (90)	398 (62)	4 (32)
C(1)	33802 (63)	17477 (36)	14286 (24)	1310 (115)	501 (38)	220 (16)	166 (102)	244 (70)	−16 (40)
C(2)	33241 (62)	27930 (35)	2424 (23)	1481 (116)	413 (35)	208 (16)	−96 (102)	348 (68)	42 (38)
C(3)	25743 (75)	21157 (37)	−10077 (24)	3084 (162)	481 (39)	151 (16)	−236 (126)	326 (80)	−4 (40)
C(4)	26864 (70)	9901 (38)	−14201 (24)	2243 (140)	566 (40)	177 (16)	4 (118)	432 (78)	38 (42)
C(5)	19071 (64)	−9522 (37)	−12644 (23)	1519 (118)	557 (38)	166 (16)	182 (108)	198 (68)	−84 (38)
C(6)	18248 (59)	−20093 (36)	−967 (24)	1117 (112)	423 (36)	265 (18)	138 (96)	156 (96)	22 (40)

were taken from Table II of Stewart, Davidson & Simpson (1965). Anomalous dispersion corrections were applied for nickel ($\Delta f'=0{\cdot}4$, $\Delta f''=1{\cdot}2$) and for chlorine ($\Delta f'=0{\cdot}1$, $\Delta f''=0{\cdot}2$).

The positions of the nickel and one chlorine were determined from an E map calculated using 230 reflections whose signs had been determined by the symbolic addition procedure (Karle & Karle, 1963). Several repetitions of Fourier syntheses yielded the positions of all the non-hydrogen atoms. Full-matrix least-squares refinement, refining all atoms anisotropically and using unit weights, reduced R to 5·8 % and R_{wtd} to 8·1 %. The weighting scheme used for the remainder of the refinement was that described by Stout & Jensen (1968). Absorption corrections were applied, reducing R to 4·9 % and R_{wtd} to 6·1 %.

A difference Fourier synthesis was calculated and yielded the positions of all 18 hydrogen atoms. Block-diagonal least-squares refinement, refining hydrogen atoms isotropically and the non-hydrogen atoms anisotropically, and applying anomalous dispersion corrections for nickel and chlorine, reduced R to 3·12 % and R_{wtd} to 4·87 %. Table 2 gives the observed and calculated structure factors for the 'observed' reflections included in the refinement.

The standard deviation of an observation of unit weight was 0·9619 after the last cycle of full-matrix least-squares refinement. This quantity is given by

$$\left(\frac{\sum w(F_o-F_c)^2}{NO-NV}\right)^{1/2}$$

where w is the weight, F_o and F_c are the observed and calculated structure factors, NO is the number of observed structure factors, and NV is the number of parameters varied during the last cycle of refinement.

The structure

All atoms lie in general positions. The positional and thermal parameters are shown in Table 3 for the non-hydrogen atoms and in Table 4 for the hydrogen atoms; the root-mean-square amplitudes for the thermal ellipsoids are shown in Table 5. The nickel atoms are in square planar configuration and lie nearly along the lines $x,0,0$ and $x,\frac{1}{2},\frac{1}{2}$ with distances of 3·621 (1) and 3·549 (1) Å between the nickels on each of these lines.

Table 4. *Hydrogen atom parameters and their estimated standard deviations*

	Positional parameter × 10^4			
	x/a	y/b	z/c	B
H(1)	2752 (57)	309 (33)	1450 (22)	3·7 (1·0)
H(2)	3857 (72)	1299 (40)	2510 (27)	6·6 (1·4)
H(3)	4364 (61)	2388 (35)	2336 (23)	4·4 (1·1)
H(4)	3895 (59)	3276 (32)	1252 (22)	3·9 (1·0)
H(5)	3497 (48)	4368 (27)	311 (18)	1·6 (0·7)
H(6)	3149 (62)	4023 (35)	−464 (24)	4·4 (1·1)
H(7)	1098 (81)	2454 (45)	−1198 (30)	8·6 (1·6)
H(8)	3676 (62)	2640 (36)	−1127 (23)	4·6 (1·1)
H(9)	4167 (53)	902 (31)	−1511 (20)	2·8 (0·9)
H(10)	1727 (59)	982 (33)	−1935 (22)	3·7 (1·0)
H(11)	2199 (66)	−580 (37)	−2273 (25)	5·3 (1·2)
H(12)	1773 (62)	−1835 (36)	−2134 (23)	4·8 (1·1)
H(13)	1335 (59)	−2531 (33)	−1080 (22)	4·0 (1·0)
H(14)	1391 (65)	−3561 (38)	−174 (24)	5·4 (1·2)
H(15)	1895 (76)	−3399 (41)	580 (28)	7·2 (1·4)
H(16)	2175 (70)	−1320 (38)	756 (26)	5·7 (1·3)
H(17)	1898 (91)	−4536 (51)	−1503 (34)	10·9 (2·0)
H(18)	−23 (84)	−4860 (48)	−1382 (33)	9·4 (1·7)

The bond lengths within the ethylenebisbiguanide-nickel(II) complex ion and the water of hydration are shown in Fig. 1; the bond angles are shown in Fig. 2.

Table 5. *Principal axes of thermal ellipsoids*

	R.m.s. amplitudes (Å)		
Ni	0·179	0·160	0·154
Cl(1)	0·244	0·237	0·179
Cl(2)	0·317	0·206	0·177
O	0·327	0·273	0·213
N(1)	0·223	0·168	0·162
N(2)	0·260	0·208	0·167
N(3)	0·239	0·180	0·152
N(4)	0·282	0·181	0·164
N(5)	0·202	0·168	0·159
N(6)	0·202	0·172	0·154
N(7)	0·277	0·207	0·161
N(8)	0·232	0·195	0·146
N(9)	0·265	0·220	0·162
N(10)	0·220	0·173	0·168
C(1)	0·193	0·181	0·166
C(2)	0·192	0·178	0·161
C(3)	0·268	0·177	0·166
C(4)	0·227	0·198	0·165
C(5)	0·206	0·181	0·161
C(6)	0·196	0·179	0·159

The bond lengths found in the isostructural ethylenebisbiguanidecopper(II) chloride monohydrate by Kunchur & Mathew (1966) are longer than those found in this study of the nickel(II) analog. A comparison of the averages of the lengths of several types of bonds determined in the two structures is shown in Table 6.

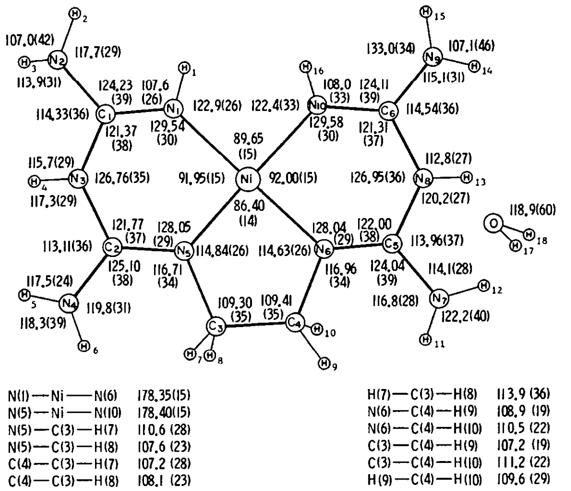

Fig. 2. Bond angles of the ethylenebisbiguanidenickel(II) complex ion and the water of hydration.

The tetradentate ethylenebisbiguanide ligand is essentially planar around the nickel. Least-squares planes were calculated using several sets of atoms within the complex ion and using unit weights for each atom. The nickel and the four coordinating nitrogen atoms lie very close to a plane; the deviation for the nickel atom is 0·0013 Å and the deviations for the nitrogen atoms are −0·0001 Å for N(1) and N(6) and −0·0005Å for N(5) and N(10). The maximum deviations (excluding hydrogen atoms) from the plane of the complex ion are ±0·16 Å for the ethylene carbon atoms; the deviations for the remaining atoms are less than 0·08 Å. The maximum deviations from the individual six-member rings are 0·04 and 0·02 Å.

Characteristics appear in the six-member rings which indicate a conjugated or 'aromatic' system. These are (1) the planarity of the rings; (2) the bond angles of approximately 120°; (3) the coordination of only three atoms around each carbon and nitrogen in the rings; and (4) the shortened C–N bond lengths and the slightly elongated C=N bond lengths. The planarity and angles of the terminal $-NH_2$ groups with respect to the six-member rings and the shortened C–N bond length together indicate that these may also be involved in the conjugation.

The work of Brown (1967) showed no distinction between double and single C–N bonds in the structure of 1-*p*-chlorophenyl-5-isopropylbiguanide hydrochloride. His C–N bond lengths ranged from 1·307 to 1·345 Å and he interpreted this as an indication of π-bonding even though the biguanide portion of the molecule was far from planar. The planarity of the six-member rings in the present compound makes it easier to speak in terms of π-bonding, delocalization, and aromaticity to explain the observed bond lengths.

Through extensive hydrogen bonding involving the water of hydration and the two chloride ions, the molecules are formed into infinite sheets parallel to the

Table 6. *Comparison of the average bond lengths in ethylenebisbiguanidecopper*(II) *chloride monohydrate with those in three studies of the nickel*(II) *analog*

	Copper(II)	Nickel(II)		
	Kunchur & Mathew (1966)	Present study	Holian & Marsh (1970)	Cogli *et al.* (1969)
Square M–N	1·965 Å	1·873 (3) Å	1·872 Å	1·858 Å
	1·961	1·859 (3)	1·858	1·853
Ring C=N	1·323	1·294 (5)	1·293	1·312
	1·323	1·284 (5)	1·286	1·295
Ring C–N	1·410	1·375 (5)	1·380	1·358
	1·410	1·367 (5)	1·369	1·359
Terminal C–N	1·369	1·344 (5)	1·343	1·332
	1·375	1·353 (5)	1·353	1·355
Ethylene C–N	1·481	1·470 (5)	1·473	1·458
Ethylene C–C	1·529	1·519 (6)	1·510	1·518

(100) planes. These sheets are perpendicular to the *c* glide and the molecules within one sheet are related to each other solely by the glide relationship. Fig. 3 shows the molecules and the hydrogen bonding in one of these sheets as projected onto the (100) plane. Fig. 4 shows the entire structure and the hydrogen bonding as projected along the *b* axis.

Hydrogen bonding

The criterion of Hamilton & Ibers (1968) was used to ascertain whether a hydrogen bond exists between two electronegative atoms. Knowing that a hydrogen atom lies approximately along the line connecting the two electronegative atoms, a hydrogen bond exists if the distance from the hydrogen to the more weakly bound atom is considerably less than the sum of the van der Waals radii.

The following van der Waals radii were obtained from Bondi (1964): Cl, 1·75 Å; 0, 1·52 Å; N, 1·55 Å; aliphatic C, 1·70 Å; aliphatic H, 1·20 Å; and aromatic H, 1·0 Å. All hydrogen bond interactions involving the water of hydration and the two chloride ions are listed in Table 7. $A\cdots B_{\text{calc}}$ and $\text{H}\cdots B_{\text{calc}}$ are the sums of the appropriate van der Waals radii; $A\cdots B_{\text{obs}}$ and $\text{H}\cdots B_{\text{obs}}$ are the experimentally-determined values. As the six-member rings appear to have 'aromatic' character, the entries in Table 7 involving hydrogens bound directly to the rings are for 'aromatic H'.

The coordination of hydrogen atoms around the oxygen is a distorted trigonal bipyramid. The atoms 0, H(14), H(17) and H(18) lie nearly in a plane with the angles

H(14)–O–H(17)	132·8 (50)°
H(14)–O–H(18)	108·3 (36)
H(17)–O–H(18)	118·6 (60)
	sum = 359·7°

The atom H(6) is in an axial position with the angles:

H(6)–O–H(14)	84·2 (15)°
H(6)–O–H(17)	89·2 (50)
H(6)–O–H(18)	99·8 (35)

The atom H(13) is considerably distorted from the axial position with the angles:

H(13)–O–H(14)	53·4 (15)°
H(13)–O–H(17)	98·8 (50)
H(13)–O–H(18)	119·3 (35)

This coordination around oxygen is very similar to that found by Ibers, Hamilton & MacKenzie (1964) in their study of sodium perxenate octahydrate in which two hydrogen atoms in a water molecule also lie in equatorial positions in a trigonal bipyramid.

One chloride ion is five-coordinate and the other is six-coordinate. This appears to be dependent on the packing rather than on any ideal coordination geometry. The positions of the hydrogen atoms in the complex ion appear to be governed primarily by

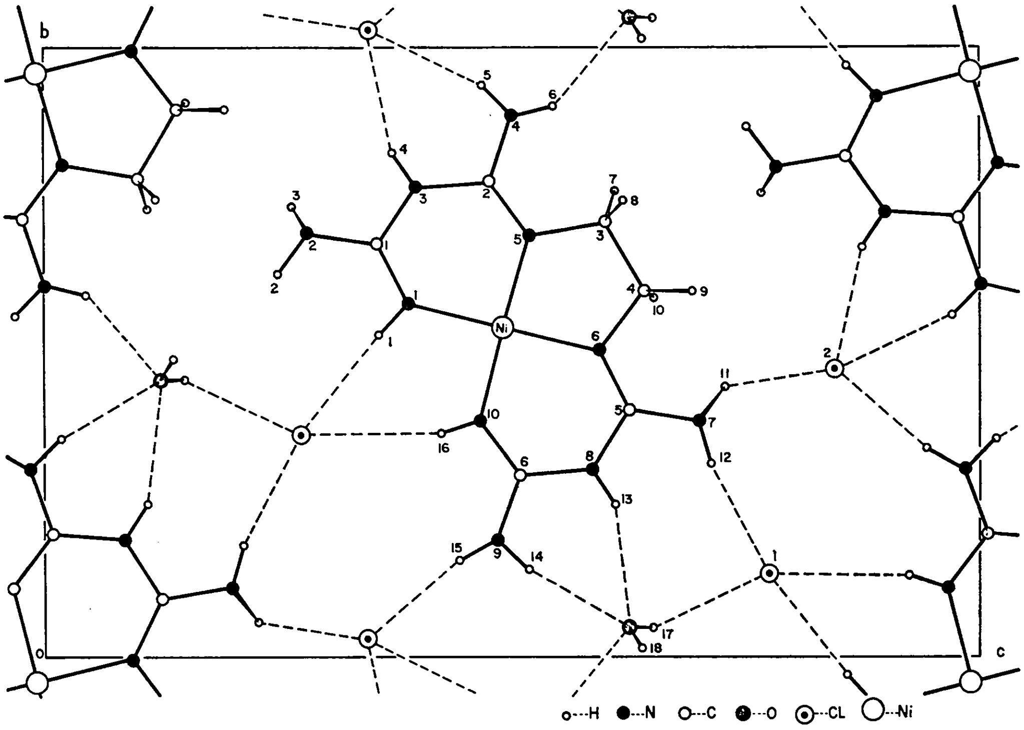

Fig. 3. Crystal structure of ethylenebisbiguanidenickel(II) chloride monohydrate projected onto the (100) plane. The molecules in one of the two layers parallel to the (100) planes are shown with the hydrogen bonds in that one layer.

the covalent bonding geometry within the complex ion. Both chloride ions have four hydrogen bonds within each sheet parallel to the (100) planes; Cl(1) has one additional bond to a hydrogen atom in an adjacent sheet while Cl(2) has two additional bonds, one each to a hydrogen atom in both adjacent sheets.

Comparison

Coghi *et al.* (1969) do not give a table of atomic positions or thermal parameters thereby leaving only bond distances (and angles) and cell dimensions for comparison. The cell dimensions determined in the present study agree with those of Holian & Marsh to within one standard deviation while they differ from those of Coghi *et al.* by two to seven standard deviations The average lengths for the different types of bonds within the complex ion are listed in Table 6 for the three studies of ethylenebisbiguanidenickel(II) chloride monohydrate and also for the isostructural copper(II) analog. Except for the ethylene C–C bond length, the present study agrees with the values of Holian & Marsh to within one standard deviation. With only three exceptions, the present study differs from the values of Coghi *et al.* by two or more standard deviations.

This pattern of agreement and disagreement is not surprising in that Coghi *et al.* obtained their data from Weissenberg films and refined their parameters to a final *R* of 9·2%, whereas Holian & Marsh used diffractometer data which refined to a final *R* of 4·8%. As the present study also used diffractometer data which refined to a low final *R*, a further comparison of the two structures is indicated.

Crystals for the two studies came from different sources. Holian & Marsh used Ni-filtered Cu $K\alpha$ radiation; the present study used Zr-filtered Mo $K\alpha$ radiation. The difference in radiations led to differences in the refinement: Holian & Marsh refined a secondary extinction parameter, applied only the real term for nickel in correcting for anomalous dispersion, and did not apply absorption corrections due to the small crystal size; in the present study, no correction for secondary extinction was made, both the real and imaginary terms for both nickel and chlorine were applied in correcting for anomalous dispersion, and absorption corrections were applied. Holian & Marsh ended their refinement when their largest parameter

Table 7. *Hydrogen bonding*

Atoms without superscript refer to the position x,y,z; (′) refers to $-x,-y,-z$; (″) refers to $\frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z$; (‴)refers to $\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z$.

Bond *A*---H···*B*	Angle *A*---H···*B*	Calculated *A*···*B*	Observed *A*···*B*	Difference *A*···*B*	Calculated H···*B*	Observed H···*B*	Difference H···*B*
N(2′) ----H(2′)·····Cl(2)	142·9 (31)	3·30	3·401 (4)	−0·101	2·95	2·613 (46)	0·337
N(3″) ---H(4″) ····Cl(2)	152·9 (40)	3·30	3·178 (4)	0·122	2·75	2·448 (38)	0·302
N(4″) ---H(5″) ····Cl(2)	157·8 (31)	3·30	3·243 (4)	0·057	2·95	2·507 (32)	0·443
N(7) ----H(11) ····Cl(2)	140·5 (37)	3·30	3·191 (4)	0·109	2·95	2·446 (44)	0·504
N(9″) ---H(15″) ···Cl(2)	163·4 (46)	3·30	3·198 (4)	0·102	2·95	2·379 (49)	0·571
O(1‴) ---H(18‴)···Cl(2)	163·3 (48)	3·27	3·230 (4)	0·040	2·95	2·300 (58)	0·650
N(1″) ---H(1″) ····Cl(1)	168·0 (37)	3·30	3·319 (4)	−0·019	2·75	2·475 (38)	0·275
N(2′) ----H(3′)·····Cl(1)	166·8 (39)	3·30	3·342 (4)	−0·042	2·95	2·595 (42)	0·355
N(7) ----H(12) ····Cl(1)	161·9 (37)	3·30	3·274 (4)	0·026	2·95	2·453 (40)	0·497
N(10″)---H(16″) ···Cl(1)	163·9 (43)	3·30	3·426 (4)	−0·126	2·75	2·650 (46)	0·100
O(1) ----H(17) ····Cl(1)	139·4 (60)	3·27	3·155 (4)	0·115	2·95	2·591 (59)	0·359
N(4) ----H(6) ·····O(1)	138·5 (40)	3·07	3·144 (5)	−0·074	2·72	2·463 (46)	0·257
N(8) ----H(13) ····O(1)	157·3 (36)	3·07	3·079 (5)	−0·009	2·52	2·308 (38)	0·212
N(9) ----H(14) ····O(1)	162·6 (41)	3·07	3·002 (5)	0·068	2·72	2·221 (42)	0·499

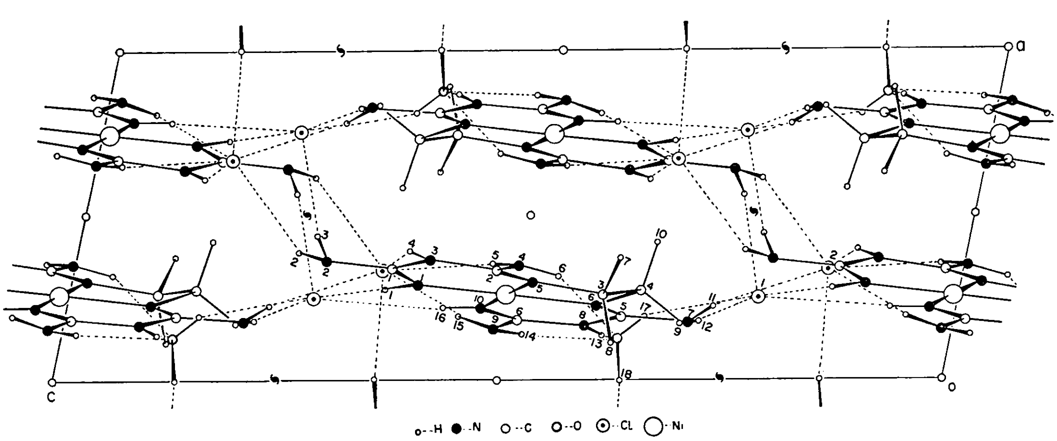

Fig. 4. Crystal structure of ethylenebisbiguanidenickel(II) chloride monohydrate projected along the *b* axis.

shift was about 0·27 times the standard deviation; the present study was refined until the parameter shifts were less than about 0·15 times the standard deviation. An additional difference between the studies was our failure to scale together the individual blocks of data (due to programming errors discovered after the present study was completed). In view of these differences between the studies, a close agreement in the final structures would reassure us of the correctness of the structures.

The average difference in the *x*, *y*, or *z* parameters for the non-hydrogen atoms is slightly less than the average of the standard deviations; no individual difference is as great as three times the individual standard deviation. The thermal parameters for the non-hydrogen atoms show close agreement. The average difference in the β_{11}, β_{22}, and β_{33} is about twice the average of the standard deviations; the magnitudes in the present study average about 5% greater. Not a single β_{12}, β_{13}, or β_{23} differs in sign and the average difference is about 0·7 times the average of the standard deviations; the magnitudes are essentially equal in the two structures.

The average difference in the *x*, *y*, or *z* parameters for the hydrogen atoms is less than 1·3 times the average of the standard deviations; four individual differences just exceed three times the individual standard deviations. Hydrogen H(17) in the water of hydration shows the greatest deviation between the two structures. The hydrogen temperature factors follow essentially the same pattern with the average in the present study being greater by nearly 20%. The standard deviations referred to above are those of the present study.

The χ^2 test (Hamilton, 1969) was applied to test the agreement between the parameters reported by Holian & Marsh and those obtained in the present study. The results are listed in Table 8. There appears to be little or no significant difference between the positional parameters of the heavy atoms; however there are significant differences in the β_{ij}'s and in the hydrogen positional parameters.* Round-off errors may contribute to the differences in that Holian & Marsh give their heavy atom parameters to only 4 decimal places and their hydrogen positional parameters to only 3.

Table 8. χ^2 *test on parameter types*

Significant values at the 0·05 level are given in parentheses.

Heavy atoms		
x	32	(30)
y	28	(30)
z	26	(30)
β_{11}	191	(30)
β_{22}	376	(30)
β_{33}	307	(30)
β_{12}	9	(30)
β_{13}	65	(30)
β_{23}	11	(30)
All positional	86	(78)
All thermal	959	(146)
All parameters	1045	(212)
Hydrogen atoms		
x	4149	(28)
y	664	(28)
z	565	(28)
B_{iso}	25	(28)
All positional	5378	(71)

A δ_p half-normal probability plot was prepared (Abrahams & Keve, 1970; Abrahams, 1970) and is shown in Fig. 5. Values of δ_{p_i} were taken as

$$\delta_{p_i}=\frac{|\text{HM Parameter}(i)-\text{WCS Parameter}(i)|}{[\sigma_i^1(\text{HM})+\sigma\,(\text{WCS})]^{1/2}}$$

where HM refers to Holian & Marsh and WCS refers to the present study.

The δ_p half-normal probability plot was interpreted (Abrahams, 1970) as follows. 'It is immediately seen that 240 of the 252 total number of parameters form a relatively linear plot, with zero intercept, and with a slope of 1·7. Assuming an equal error distribu-

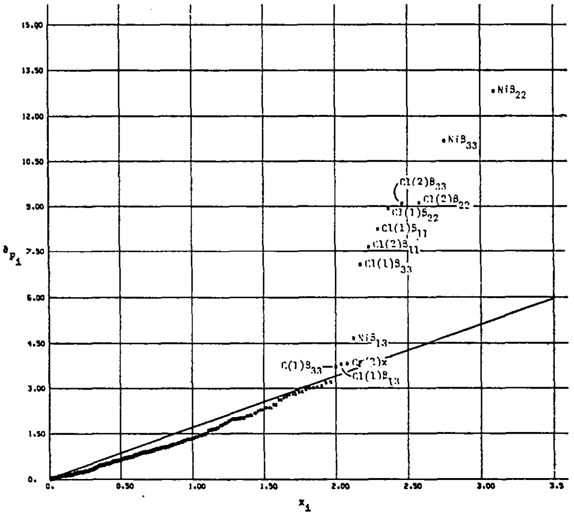

Fig. 5. Half-normal probability plot of 252 δ_{p_i} derived from the comparison of the atom parameters reported by Holian & Marsh (1970) and those of the present study.

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* As a systematic error in the intensity data could conceivably lead to such differences, especially in the β_{ij}'s, the data were re-reduced (this time applying the proper scaling), the absorption correction was applied, and 4 cycles of block-diagonal least-squares refinement were applied leading to a final *R* of 2·87%. The χ^2 test was applied to compare these parameters with those of Holian & Marsh. The agreement of a few parameter types (β_{11} and hydrogen *y*) were improved but the apparent overall agreement was reduced.

A possible explaination for this phenomenon requires an examination of the mathematical procedure. As the parameters in the present study are further refined with a data set which is free from systematic errors, the estimated standard deviations become smaller. The standard deviation of the difference then becomes smaller and the weighted difference becomes larger for an equal unweighted difference [see equations (13) and (12), respectively, of Hamilton (1969)]. Thus the χ^2 test would be likely to show poorer agreement with further refinement if the one structure did not refine towards the other's parameters.

tion in the HM and WCS standard deviations, this can only mean that both determinations have underestimated these standard deviations by a factor of 1·7. The additional 12 parameters are, with two exceptions all heavy atom thermal parameters. These clearly belong to a different distribution from the first 240 parameters (which in fact include the hydrogen parameters). A simple, and probably only partially correct, interpretation is that these 10 heavy atom thermal parameters belong to a distribution with a slope of 3·6, *i.e.* that these all have estimated standard deviations too small by a factor of 3·6. It is probably more correct to say that these parameters are characterized by a non-normal random error distribution, with highly systematic errors either in the parameters themselves or in their standard deviations'.

The good agreement with the results of Holian & Marsh, with respect to the heavy atom positional parameters, indicates that both determinations of the overall structure are likely to be correct.

The differences in thermal parameters and in the hydrogen parameters may be attributed to errors in one or both sets of data, or to failures to apply necessary corrections to the data, or to incomplete refinement. The data set in the present study may be suffering from coincidence loss errors in the strong intensities. Holian & Marsh did not apply an absorption correction to their intensity data. The present study was refined far beyond normal limits, even though the shifts were relatively small and the R value was not improving significantly, since some hydrogen atoms continued to have parameter shifts consistently in the same direction.

It appears likely that, by applying absorption corrections to the data of Holian & Marsh and by eliminating errors in the strong intensities in the present study followed further refinement of both sets of parameters, the agreement between the two sets of parameters would show considerable improvement.

We wish to acknowledge the National Aeronautics and Space Administration fellowship to D. L. W. while working on this research. We also wish to thank Miss Anne C. Baker and Mrs Margaret A. Hurley for their care in collecting the intensity data, Mrs Grace France for preparing the projection drawings, the Montana State University Computing Center for a grant of computing time, Dr Richard E. Marsh for sending a preprint of the paper by Holian & Marsh and Dr S. C. Abrahams for preparing the δ_p plot, its interpretation, and for his helpful discussions.

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