Acta Cryst. (1959). **12**, 24

The Crystal Structure of Nickel Etioporphyrin II

By M. B. Crute*

Crystallographic Laboratory, The Johns Hopkins University, Baltimore 18, *Maryland, U.S.A.*

(*Received* 20 *January* 1958 *and in revised form* 15 *July* 1958)

Crystals of nickel etioporphyrin II are tetragonal or twinned-orthorhombic, pseudo-tetragonal, with $a = 14{\cdot}6_8$, $c = 12{\cdot}5_1$ Å. The space group appears to be $I4_1/amd$ with $Z = 4$. From data obtained at room temperature a structure has been deduced which yields $R = 0{\cdot}24$ for 132 non-zero reflections. The structure has 15 parameters, excluding those for hydrogen. Flat molecules, related by a 4_1 axis, lie with their mean planes parallel to (001) at heights $\frac{1}{8}$, $\frac{3}{8}$, $\frac{5}{8}$, and $\frac{7}{8}$. The Ni atoms lie upon sites of symmetry $\bar{4}m2$ with the Ni–N bonds in mirror planes {100}. By random distribution, enantiomorphous molecules acquire a statistical symmetry not inherent in the individual molecule. A rapid decline of intensities with increasing 2θ, which drastically limits the number of observed reflections, leads to abnormally high, anisotropic 'temperature factors'. The magnitude of these factors is ascribed to disorder.

Experimental

The crystals of nickel etioporphyrin II, $C_{32}H_{36}N_4Ni$ (Fig. 1), were prepared by Dr Winslow Caughey. They are very soft, opaque, tetragonal dipyramids {101}, pseudo-octahedra, 0·05 to 0·10 mm. on an edge. They are deep purple with vitreous luster, and very thin fragments weakly transmit red light. The material decomposes in the solid state at approximately 350 °C.

Using Cu $K\alpha$ radiation, precession photographs were taken of reciprocal-lattice nets containing the reflections $hk0$, $h0l$, $hk1$, and hhl. Cell dimensions obtained from these photographs are:

$a = 14{\cdot}6_8$, $c = 12{\cdot}5_1$ Å. The cell volume is 2696 Å^3.

No single crystal was large enough for its density to be determined on the Berman balance, and the total quantity of crystals available was insufficient for a pycnometric determination. By flotation in $Ni(NO_3)_2$ solutions, a value of $\varrho = 1{\cdot}5 \pm 0{\cdot}2$ g.cm.$^{-3}$ was obtained. With $Z = 4$, the calculated density is 1·37 g.cm.$^{-3}$.

Within the limits of visual observation, reflections hkl, khl, $\bar{k}hl$, and $h\bar{k}l$ have equal intensities (to within $\pm 10\,\%$) so that the Laue class is taken as $4/m, 2/m, 2/m$. The space group is then uniquely determined by the following conditions for reflection:

hkl: $(h+k+l)$ even
$hk0$: h and k even
hhl: $(2h+l)$ even .

The multiplicity of the general position is 32.

Equi-inclination Weissenberg photographs of nine levels perpendicular to the c axis were taken with Cu $K\alpha$ radiation. Exposures of 36 to 60 hours were necessary. Trial exposures for longer periods failed to yield additional reflections. Three films were used, and intensities were measured on an arbitrary scale by visual comparison with a calibrated strip prepared using the same crystal. The collimator aperture was 1 mm. No diffuse background was observed except for a possible elongation of spots in the [001] direction which is difficult to distinguish from an elongation always present due to some back-lash in the camera used. There are 952 possible reflections in the region of reciprocal space covered by the photographs taken. Reflections were obtained only out to $\theta = 48°$ which limit encompasses 309 possible reflections. Only 138 of these reflections were observed at room temperature. Lorentz-polarization corrections are applied. In view of the small size of the crystal, about 0·05 mm., absorption corrections are omitted.

Determination of the structure

The C atoms are numbered in Fig. 1. The molecule is

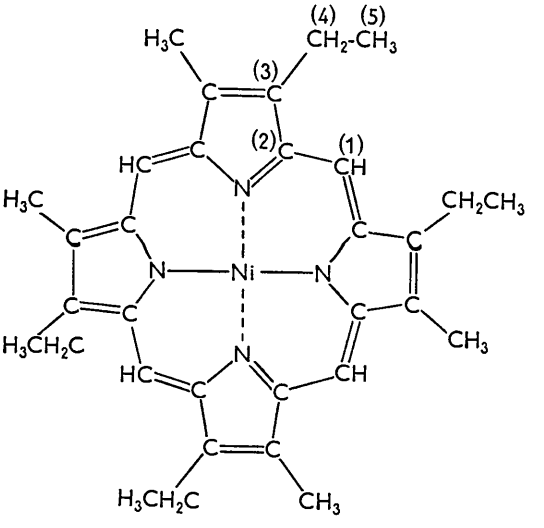

Fig. 1. Nickel etioporphyrin II.

* Present address: Department of Metallurgical Research Kaiser Aluminum & Chemical Corp. Spokane 69, Washington.

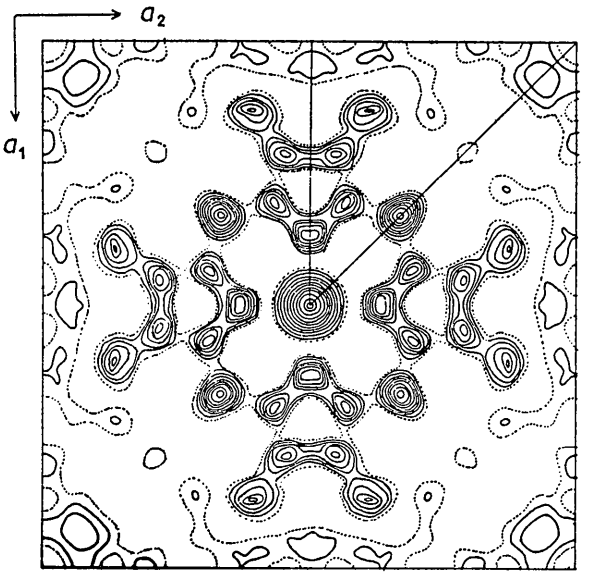

Fig. 2. Patterson section at $Z = 0$. Contoured at arbitrary intervals. Origin is at the center of the square.

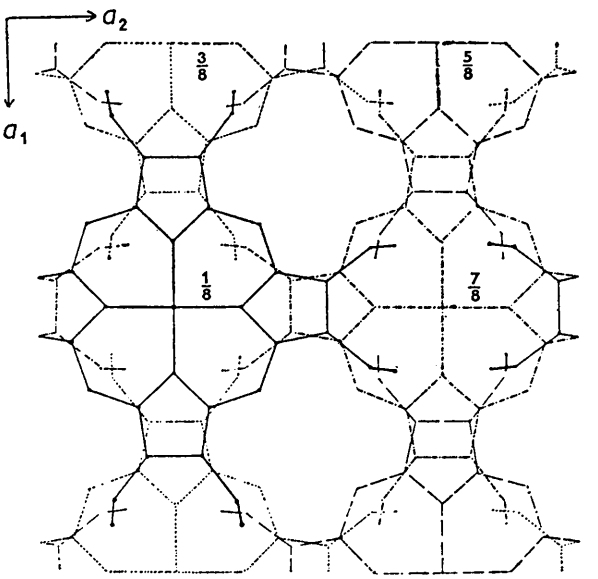

Fig. 4. The structure projected on (100). The C_5 atoms are half-atoms.

initially assumed to be planar and the origin of the cell is placed at a center of symmetry at distances $0, -\frac{1}{4}, \frac{1}{8}$ from site $\bar{4}m2$. The space group requires that the four Ni atoms occupy position b (or a, equivalent by a change of origin) of multiplicity 4. The symmetry of the sites is $\bar{4}m2$. A study of the space group reveals that, within the assumptions made about the shape of the molecule, one only need consider two possible orientations of the molecules. The molecules, related by a 4_1 axis, must lie parallel to (001) with their Ni atoms at $(\frac{1}{2}, \frac{1}{4}, \frac{1}{8})$, $(0, \frac{1}{4}, \frac{3}{8})$, $(0, \frac{3}{4}, \frac{5}{8})$, and $(\frac{1}{2}, \frac{3}{4}, \frac{7}{8})$. The space-group conditions for the $hk0$ reflections amount to a halving of a_1 and a_2 in basal projection, so that the basally projected molecules must be translation-equivalent. The two possible orientations of the molecules differ only by a 45° rotation in the horizontal plane. The pyrrole rings may be directed along the a directions or along the directions of the base diagonals; i.e. either the C_1 atoms lie upon the 2-axes (position g) and the N atoms lie in the vertical mirrors (position h), or *vice versa*.

The basally projected molecules must have symmetry $4ll$. The heavy Ni atoms and the mean planes of the molecules lie at heights $\frac{1}{8}, \frac{3}{8}, \frac{5}{8}$, and $\frac{7}{8}$, parallel to (001) with only one molecule at each of these heights. For these reasons the Patterson section at $Z = 0$ shows an image of the planar part of the molecule (Fig. 2). The Patterson section also shows that the N atoms occupy sites in the vertical mirrors and the C_1 atoms lie on the 2-axes.

Note that, owing to the presence of an ethyl group on each pyrrole ring, the symmetry of the projected molecule (Fig. 1) is not $4ll$, as required by the space group, but $ll2$, or lower, depending on the configuration of the C_5 atoms. Stating the problem in another way: there are only sixteen C_5 atoms in a space group of multiplicity thirty-two and they cannot be placed into any special position without unreasonable distortion of normal bond lengths and angles. The only alternative is to place $\frac{1}{2}$ C_5 in general position. Physically, this means that the molecules are equally divided between two enantiomorphous configurations and that, being randomly distributed, they assume a statistical symmetry $\bar{4}2m$ (Fig. 3).

Fig. 4 shows the structure projected on (001). The

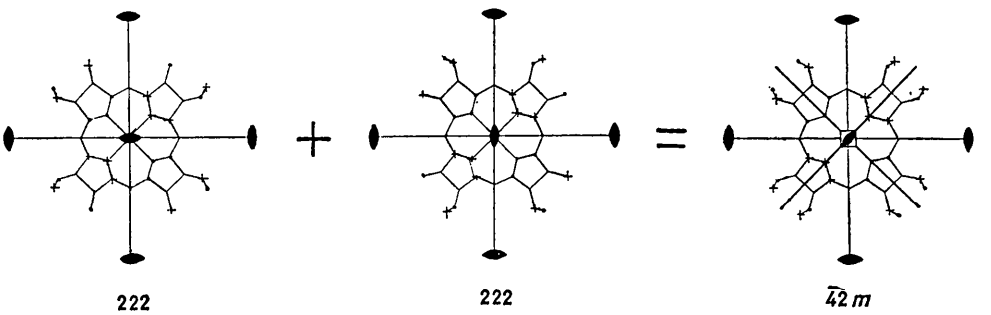

Fig. 3. Statistical symmetry of the molecule. The C_5 atoms in the molecule at the right are half-atoms.

fundamental domain selected is bounded by the five planes: $z = 0$, $z = \frac{1}{4}$, $y = \frac{1}{4}$, $x = 0$, and $x+y = \frac{3}{4}$.

An approximate structure, using rough coordinates obtained from the Patterson section, was used to calculate structure factors, omitting C_5, making no temperature corrections, and placing all atoms in the fundamental domain at $z = \frac{1}{8}$. These structure factors yield $R \sim 0{\cdot}45$, where $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$. On the basis of this calculation signs were given to most of the observed F's and an electron-density section at $z = \frac{1}{8}$, similar to the one shown in Fig. 5, was computed. F's recalculated using x, y coordinates obtained from the E.D. section, placing all atoms in the fundamental domain at $z = \frac{1}{8}$, excluding zero reflections, omitting C_5 atoms, and applying an isotropic temperature correction with $B = 4{\cdot}8$ Å^2, yield $R = 0{\cdot}35$.

A plot of $\ln(F_c^\circ/F_o)$ versus S^2, where $S = (\sin\theta)/\lambda$ and F_c° is the structure factor calculated using the theoretical scattering factors, is completely unsatisfactory for obtaining temperature corrections, indicating a pronounced anisotropy; moreover, the magnitude of the temperature corrections indicates a disorder. Numerous attempts, not discussed here, were made to modify the structure within reasonable limits so that these corrections would be reduced to a more reasonable magnitude and to obtain better agreement between observed and calculated F's. Attempts at improvement of the situation were finally abandoned.

Table 1. *Trimetric coordinates of the atoms in the fundamental domain*

Atom	x	y	z	Position	
$\frac{1}{8}$ Ni	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$4b$	$\bar{4}m2$
$\frac{1}{2}$ N	0·375	$\frac{1}{4}$	0·122	$16h$	m
$\frac{1}{2}$ C_1	0·342	$\frac{3}{4}-0{\cdot}342$	$\frac{1}{8}$	$16g$	2
C_2	0·311	0·316	0·119	$32i$	1
C_3	0·217	0·300	0·125	$32i$	1
C_4	0·137	0·363	0·133	$32i$	1
$(\frac{1}{2}C)_5$	0·089	0·366	(0·023)	$32i$	1

Table 2. *Calculated and observed structure factors*

The scale factor, s, is given for each level

hkl	$\|F_o\|$	F_c
(s = 0·87)		
200	83	104
220	69	52
400	96	−75
420	50	−46
440*	139	137
600	73	61
620	58	−63
800	37	45
820	57	−74
660	41	−44
860	30	−31
10,2,0	44	−53
880	52	58
12,6,0	20	14
14,0,0	17	16
14,2,0	16	−11
(s = 1·07)		
101*	171	−260
211	17	9
301	66	−49
321	26	21
411	61	−49
501	61	−55
431	20	39
521	24	49
611	67	−74
541	20	1
701	25	−44
721	58	58
741	35	−23
811	19	−21
831	33	38
761	31	34
921	20	33
851	26	−24
10,3,1	20	18
11,0,1	36	−21
11,2,1	18	24
(s = 0·84)		
112	73	104
202	20	4
312	53	85
332	47	−27
512	76	96
532	8	− 1
712	67	60
552	31	−14
732	56	−56
752	39	31
932	30	−40
772	40	−30
952	22	15
11,1,2	41	37
992	27	31
(s = 0·82)		
103*	123	258
213	29	10
303	16	55
323	13	−24
413	12	−27
433	58	26
503	16	17
523	32	−30
613	66	−59
543	20	18
703	30	28
723	55	−49
743	16	28
813	30	−24
833	20	36
923	30	−30
763	29	−30
10,3,3	23	25
873	27	28
11,0,3	26	26
11,2,3	21	−23
983	25	20
(s = 0·89)		
004*	110	−375
204	46	−42
224	27	49
314	12	−13
404	34	−27
424	45	51
444	42	−56
604	69	−75
624	54	54
824	46	27
664	37	23
844	20	− 5
864	29	33
10,0,4	23	−16
10,2,4	35	36
884	35	−46
(s = 0·82)		
105†	57	170
215	15	13
305	18	24
325	26	−18
415	24	28
435	20	−25
505	29	20
525	15	−25
615	39	42
725	39	−33
705	27	22
745	25	19
835	21	−25
765	25	−25
875	12	−20
11,0,5	24	17
985	16	19
(s = 0·74)		
116†	31	−60
206	35	5
316	21	−35
336	22	22
516	36	−32
606	17	− 2
716	33	−32
736	27	31
756	20	−22
936	17	22
776	24	17
11,1,6	21	−22
(s = 1·08)		
107	43	−46
417	9	27
437	29	−23
507	17	−23
617	27	29
707	17	20
727	26	22
817	15	14
837	11	−18
927	22	12
10,1,7	16	9
877	21	−14
(s = 0·77)		
008	85	90
208	19	22
408	14	8
428	15	−15
608	26	27
628	21	−21
828	20	−17

* High intensity reflections omitted from computation of R.
† Reflections in proximity to shadow of beam catcher, omitted.

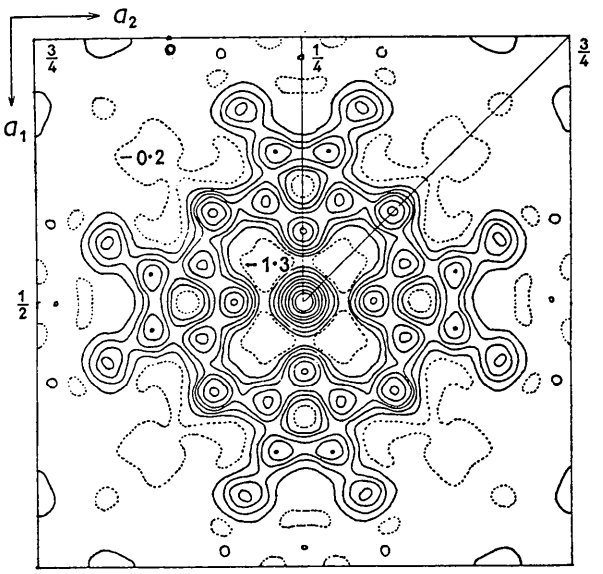

Fig. 5. Electron-density section at $z = \frac{1}{8}$. Contoured at intervals of 0·5 e.Å^{-3}, except for Ni which is contoured at intervals of 2 e.Å^{-3}. Zero contour is broken. Origin at 0.

Difference syntheses proved unsuccessful, apparently due to uncertainty in the scale of F_o.

Successive computation of the E.D. section at $z = \frac{1}{8}$ and re-calculation of F failed to reduce R. The form of 'temperature correction' used was predominant in determining the extent of agreement. On the basis of polar-coordinate plots of $(1/S^2) \ln (F_c^\circ/F_o)$ versus φ, where φ is the angle between the reciprocal-lattice vector and the c axis, an ellipsoid of revolution about c was taken as a reasonably good representation of the configuration of B. With this modification, the F's were calculated and put into the sign determination for an E.D. section at $z = \frac{1}{8}$. The coordinates from this section were used in one further calculation of F. The observed F's were re-scaled separately for each level and the final section shown in Fig. 5 was computed. The coordinates reported in Table 1 are taken from this section and from line sections passed, parallel to c, through atoms C_2, C_3, C_4, and N. The x, y coordinates for C_5 are those which give the best agreement for the $hk0$ reflections and the z coordinate is chosen to give the best agreement with normal bond-lengths and angles. Structure factors calculated from these coordinates are given in Table 2. The following form was used for the correction of scattering factors:

$$f_j = f_j^\circ \exp\left[-\alpha_j S^2/(1+\beta_j \sin \varphi)\right]$$

where f_j° is the theoretical scattering factor for atom j. The scattering factor of nickel is corrected for dispersion (Dauben & Templeton, 1955). The values of α and β used were as follows:

$\alpha_{Ni} = 10{\cdot}6$ Å^2	$\beta_{Ni} = 0{\cdot}90$
$\alpha_N = 12{\cdot}2$	$\beta_N = 0{\cdot}43$
$\alpha_C = 13{\cdot}8$	$\beta_C = 0{\cdot}43$

The value of R is 0·24 for the observed reflections when a scale factor, s, is obtained for each level (see Table 2). The approximate bond lengths obtained from these coordinates are given in Table 3.

Table 3. *Interatomic distances*

Intramolecular	
Ni–N	1·84 ± 0·03 Å
N–C_2	1·35 ± 0·05
C_1–C_2	1·43 ± 0·05
C_2–C_3	1·40 ± 0·05
C_3–C_3	1·47 ± 0·08
C_3–C_4	1·50 ± 0·05
Intermolecular	
C_2–C_3'	3·23 ± 0·05
C_1–C_4'	3·25 ± 0·05
C_3–C_3'	3·27 ± 0·05

The fact that the peak heights in the electron-density section are much lower than expected is attributed to the high 'temperature corrections'.

Discussion of the structure

The Fourier syntheses obtained leave little doubt as to the essential correctness of the proposed structure; however, it is evident that a refined structure cannot be obtained from the limited number of reflections. Hope of bringing the value of R down to the magnitude of uncertainty in intensity measurements, about 15%, did not materialize. It was necessary to take anisotropic corrections into consideration almost from the start in order to bring R down to 0·24.

The z coordinates shown in Table 1 indicate a slight departure of the molecule from planarity which cannot be confirmed at this point.

Reflection criteria in the orthorhombic space group *Fddd* are the same as in the tetragonal space group $F4_1/ddm$ into which $I4_1/amd$ can be transformed by matrix $110/\bar{1}10/001$. The possibility of an orthorhombic pseudo-tetragonal crystal should therefore be considered. *Fddd* is completely compatible with the symmetry 222 of the molecule.

Due to uncertainties about film shrinkage, a decision as to tetragonality or pseudo-tetragonality could not be reached on the basis of film measurements. An attempt was made to account, in the orthorhombic hypothesis, for the apparent Laue symmetry $4/m, 2/m, 2/m$. The reflections most sensitive to the placing of C_5, either on one side of the pyrrole ring or the other, are the tetragonal reflections hhl, which become $H0L$ in orthorhombic indexing.

The contribution of C_5 in the proposed orthorhombic structure was calculated by placing that atom in general position in *Fddd* with coordinates corresponding to those used in $I4_1/amd$. *Fddd* generates only one C_5 for each pyrrole ring. Values of F were calculated for some $H00$ and $0H0$ reflections, but these do not even approximately show the tetragonal symmetry—

Table 4. *Calculation of some structure factors in four hypotheses*

Hypothesis	Method of calculation of F	Result
(1) Tetragonal	$\frac{1}{2}$ C_5 placed in general position in $I4_1/amd$	$R = 0{\cdot}20$
(2) Orthorhombic pseudo-tetragonal	C_5 placed in general position in $Fddd$ using coordinations corresponding to those in (1)	Calculated F's do not comply with observed Laue symmetry
(3) Orthorhombic twin	$\lvert F_c\rvert = (F_1^2+F_2^2)^{\frac{1}{2}}/\sqrt{2}$, where F_1 is calculated as in (2) and F_2 is calculated from the same structure reflected in (110)	$R = 0{\cdot}20$
(4) Combination (1) and (3)	F taken as average of that calculated from (1) and (3)	$R = 0{\cdot}17$

even when considerably reduced in magnitude by applying the abnormally large 'temperature corrections'. No coordinates for C_5 could be found which would remove the discrepancies between F_{H00} and F_{0H0}.

The above considerations suggest that twinning of the orthorhombic (pseudo-tetragonal) crystal, say by reflection in (110), might bring about the required tetragonal symmetry of the reflections. The orthorhombic-twin hypothesis implies perfectly ordered domains of at least a few hundred cells, in which the space group $Fddd$ applies.

The tetragonal-crystal hypothesis implies random distribution of right-handed and left-handed molecules even within a single cell.

The structure factors obtained by averaging those from the two hypotheses correspond to a third possibility: a combination of the two, i.e. domains of orthorhombic individual 1 and of orthorhombic individual 2 with interspersed cells having the random disposition of C_5. Structure factors calculated for the various possibilities were compared for twenty reflections (Table 4).

The author wishes to express his appreciation for the guidance and instruction he received from Prof. J. D. H. Donnay and from Dr Gabrielle Donnay. Thanks are also due to Prof. Alsoph H. Corwin and Dr Winslow S. Caughey for their interest in this work.

This study has been made possible by the support of the National Science Foundation.

Reference

Dauben, C. H. & Templeton, D. H. (1955). *Acta Cryst.* **8**, 841.

Acta Cryst. (1959). **12**, 28

The Crystal Structure of Ruthenocene*

By George L. Hardgrove and David H. Templeton

Department of Chemistry and Radiation Laboratory, University of California, Berkeley, California, U.S.A.

(*Received* 23 *June* 1958)

Dicyclopentadienylruthenium, or ruthenocene, crystallizes in the orthorhombic space group $Pnma$ with $a = 7{\cdot}13$, $b = 8{\cdot}99$, $c = 12{\cdot}81$ Å. There are four $Ru(C_5H_5)_2$ molecules per unit cell. The ruthenium atoms form approximately a face-centered lattice, and the cyclopentadienyl rings lie in an eclipsed configuration with respect to each other about each ruthenium atom. The structure was refined by Fourier and least-squares methods with 791 independent reflections. The ruthenium–carbon distance is 2·21 Å and the carbon–carbon bond distance in the rings averages 1·43 Å.

Introduction

X-ray investigation by Fischer and his collaborators (Pfab & Fischer, 1953, Weiss & Fischer, 1955) indicated that the dicyclopentadienyl compounds of iron, cobalt, nickel, chromium, vanadium and magnesium are isomorphous, crystallizing in space group $P2_1/c$. Dunitz, Orgel & Rich (1956) have reported a three-dimensional analysis of the iron compound. The present paper reports a three-dimensional analysis of dicyclopentadienylruthenium, which unexpectedly was found to have a quite different orthorhombic structure.

* This research was supported by the U.S. Atomic Energy Commission.