molar ratio Be/Be + citric acid was 0.65, which is sufficiently close to the theoretical value of 0.67 to establish the existence of a stable, soluble beryllium-citrate complex at pH 8.25 having a beryllium to citrate combining ratio of two. Undoubtedly, none of the beryllium in this complex is ionic since any ionic beryllium would precipitate at this pH.

It should be noted that this method gives no information concerning the existence of a complex having a Be/citrate ratio less than two, but only establishes the maximum number of beryllium atoms bound by one citrate ion, since only the total concentration of dialyzable beryllium, rather than a physical property of one particular complex, is measured.

The stability of the 2:1 complex decreases rapidly above pH 8.5. This pH effect is shown by Fig. 3. The increased diffusibility of beryllium at pH 11is probably due to the formation of beryllate ions.¹⁰

The complexing action of citrate ions on beryllium in the system beryllium chloride-citrate-bicarbonate at pH 8 is dependent on the order of mixing the constituents. The maximum concentration of dialyzable beryllium reported above, $94 \pm 4\%$, was obtained only when the beryllium chloride and citric acid were mixed *before* the solution was made alkaline. When sodium citrate was added to beryllium chloride in the molar ratio of Be₂R and the *p*H was raised to 8.3, duplicate experiments showed that only $82 \pm 3\%$ of the beryllium was dialyzable after four days. It seems, therefore, that even though the citrate is a very strong complexer for beryllium and even though the

(10) N. V. Sidgwick, "Chemical Elements and Their Compounds," Oxford University Press, London, 1950, p. 202.



Fig. 3.—Effect of pH on diffusibility of beryllium in mixture containing beryllium and citrate in molar ratio of two: total Be concentration, $1.9 \times 10^{-4} M$; ionic strength (NaHCO₁ concentration), 0.025 M; room temperature; duration of dialysis, 4 days.

citrate/hydroxyl ratio in these mixtures was 10^5 , beryllium reacts more rapidly with hydroxyl ions than with citrate ions but that in the presence of sufficient citrate the beryllium hydroxide is solubilized in time. As was to be expected, then, when citric acid was added to a mixture of beryllium chloride in 0.025 *M* bicarbonate and the *p*H was raised to 8.3, slightly less beryllium was dialyzable, $77 \pm 5\%$.

ROCHESTER, N. Y.

RECEIVED MARCH 15, 1951

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Structure of Thorium Dicarbide by X-Ray and Neutron Diffraction¹

BY ELTON B. HUNT AND R. E. RUNDLE

Good-X-ray powder diagrams show that ThC₂ is not tetragonal, as previously reported. Single crystals have been obtained, and the lattice has been established as C-centered monoclinic with $a_0 = 6.53$, $b_0 = 4.24$, $c_0 = 6.56$ Å., $\beta = 104^\circ$, Z = 4. The space group is C2/c or Cc. Thorium positions, determined by X-ray diffraction, are the same in either group, and satisfactory carbon positions have been found in C2/c by neutron diffraction.

The structure contains C_2 groups, but the C-C distance is about 1.5 Å., so that acetylene ions are eliminated. The arrangement of thoriums about the C_2 group combines ethane-like, ethylene-like and acetylene-like character, and considerable covalent character for the Th-C bonds is indicated.

Introduction

The tetragonal structure proposed for ThC_2 by von Stackelberg² on the basis of powder diffraction data has been one of the classical type structures for the dicarbides for 20 years. In suggesting carbon positions for ThC_2 , von Stackelberg assumed C_2^- ions were involved, and it has generally been supposed that these were acetylene ions, such as those found in CaC_2 .

Good powder data show that the correct structure for ThC_2 cannot be based on a tetragonal lat-

(1) Contribution No. 111 from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa. Work performed in the Ames Laboratory of the Atomic Bnergy Commission.

(2) von Stackelberg, Z. physik. Cham., [B] 9, 487 (1980).

tice.³ Recently, with the help of Mr. F. J. Modic and Dr. Premo Chiotti we have been able to secure single crystals, and have found the true lattice and thorium positions by X-ray diffraction. In addition, rough carbon parameters have been determined by neutron diffraction.

Preparation of Single Crystals.—Thorium dicarbide single crystals were prepared by the extended heating of thorium metal surrounded by graphite at 2000–2500°. A ThC₂ diffusion band forms in such samples, and in favorable cases crystals as large as a mm. in cross section were found. Most crystals were highly twinned, but upon polishing and optical observation of lumps from these

(8) N. C. Baengizer, unpublished research, Ames Laboratory of the A.B.C.

bands, small single crystals suitable for X-ray work were obtained. Crystals were examined and mounted in thin-walled capillaries, keeping them covered with molten petroleum jelly which solidified in the capillaries to hold the crystals in place. The identity of the crystals was established as ThC_2 by powdering crystals from the band, and comparing powder patterns with authenticated ThC_2 .

X-Ray Data and Thorium Positions.—Single crystal precession diagrams of ThC_2 exhibited apparently orthogonal axes with $a_0 = 8.05$, $b_0 =$ 4.24, and $c_0 = 10.31$ Å. However, the *n*-level symmetry, obtained by precession about the *a*-axis and the *c*-axis, was only C_l , and about the *b*-axis, only C_2 , showing that the Laue symmetry is C_{2h} . Thus the crystal is monoclinic rather than orthorhombic.

The smallest monoclinic cell is C-centered with $a_0 = 6.53$, $b_0 = 4.24$, $c_0 = 6.56$ Å. and $\beta = 104^{\circ}$. The density calculated on the basis of 4 ThC₂ per unit cell is 9.6; P (pycnometer) is 9.5 \pm 0.5.

Single crystal pictures were obtained using a precession camera $(\mu - 30^{\circ})$ and Mo characteristic K radiation. Intensities of the (hk0) and (0kl) reflections were obtained by visual estimation of timed exposures of sets of 5 precession films with an exposure factor of 3 between successive films. A G.E. XRD-3 unit with regulated voltage and current was used for these exposures. The relative intensities were converted to F² by correcting for polarization and for the Lorentz factor by the method of Buerger.⁴ The temperature factor is negligible over the sphere of reflection studied and was omitted, and, since the crystals used were irregular-shaped fragments, no absorption corrections could be made.

Two systematic absences were observed: (hkl)absent for h + k = 2n + 1, and (h0l) absent for l = 2n + 1, indicating C-centering and c-glide plane, respectively. The space group, therefore, is C2/cor Cc, differing only in that the former is centrosymmetric and the latter is not.

The space group C2/c has only 4-fold and 8-fold sets of positions. In this group the 4-fold sets are

dd	(0,0,0; 3,3,0)) t o e a	ch position	below]
	4(a)	0,0,0;	$0, 0, \frac{1}{2}$	-
	4(b)	$0,\frac{1}{2},0;$	$0, \frac{1}{2}, \frac{1}{2}$	
	4(c)	$\frac{1}{4}, \frac{1}{4}, 0;$	$\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$	
	4(d)	$\frac{1}{4}, \frac{1}{4}, \frac{1}{2};$	ī, 1 ,0	
	4(e)	0,y, ¹ / ₄ ;	$0, \overline{\mathbf{y}}, \overline{\frac{1}{4}}$	

[A]

Sets (a) and (b) are body-centered positions and since reflections with (k + k + l) odd are no weaker, as a class, than other reflections the thorium atoms cannot be in either set. Sets (c) and (d) are eliminated in a similar manner since the reflections do not indicate face-centered thorium positions, as required by these sets. The only set remaining in space group C2/c is (e).

Space group Cc contains only the general set: x, y, z; x, y, $\frac{1}{2} + z$; $\frac{1}{2} + x$, $\frac{1}{2} + y$, z; $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$. This set reduces, without loss of generality, to set (e) of space group C2/c by proper choice of the origin ($x = 0, z = \frac{1}{4}$). Thus, in the

(4) M. J. Buerger, "The Photography of the Reciprocal Lattice," ASXRED Monograph No. 1, The American Society for X-Ray and Electron Diffraction, Cambridge, Mass., 1944. location of the Th atoms, only the set of positions (e) need be considered.

The approximate Th parameter was obtained from the Patterson projections, P(xy) and P(yz). These projections also substantiated the conclusion, in the last paragraph, that the Th atoms are in set (e). P(xy) exhibited large peaks at $\pm (0, 0.4)$ and $\pm (0.5, 0.9)$ while P(yz) exhibited large peaks at $\pm (0.4, 0.5)$ and $\pm (0.9, 0.5)$. The Th parameter, as given by each of these projections, is, therefore, $y_{\rm Th} = 0.2$. Fourier projections onto (001) and (100) planes confirmed the thorium parameter but gave no hint of the carbon positions.

The Th parameter was refined and limits placed on it by comparing rather carefully selected pairs of adjacent (hk0) reflections for which absorption must be nearly equal since, as pointed out earlier, no correction for absorption could be made. The intensity relationships between the pairs of adjacent reflections which were used to set the lower limit on y_{Th} are

T 620	>	I_{730} requires $y_{\rm Th} > 0.194$
1620	>	l_{530} requires $y_{\rm Th} > .197$
I 620	≥	$9I_{710}$ requires $y_{\rm Th} > .200$
1830	>	$9I_{440}$ requires $\gamma_{Th} >198$

The upper limit on the Th parameter was set by

 $I_{333} > 3I_{240}$ requires $y_{Th} < 0.205$ $I_{150} > 3I_{240}$ requires $y_{Th} < .207$

The carbon contribution, even though it was small, was included in the above calculations, using the carbon positions given in the next section. On the basis of the above calculations, it appears that $y_{\text{Th}} = 0.202 \pm 0.003$.

Table I gives the calculated and observed values of the structure factors for the (hk0) and (0kl) reflections. The $F_{\text{calcd.}}$ values are for $y_{\text{Th}} = 0.202$, and $x_C = 0.290$, $y_C = 0.132$, $z_C = 0.082$. The in-

TABLE	Ι
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Calculated and Observed Values of the Structure Factors for (hk0) and (0kl) X-Ray Reflections

hk0	Fealed.	Fobsd.	0kl	Fcaled.	$F_{\rm obsd}$
200	73	96	002	-73	117
400	68	72	004	6 0	86
600	51	73	006	-60	61
800	45	50	008	42	22
110	23	16	020	-60	47
310	23	24	021	-46	42
510	15	16	022	55	53
710	16	18	023	26	31
020	-60	41	024	-47	55
220	-55	61	025	-35	46
420	- 48	50	026	42	45
62 0	-41	47	027	29	16
820	-35	41	040	15	^a
130	-47	38	041	49	52
3 30	-46	49	042	-21	35
530	-37	43	043	-46	49
730	-37	36	044	20	13
040	15	14	045	43	39
2 40	21	24			
440	15	16			
150	47	35			
350	44	38			

" Could not estimate due to interference from twinning.

dex $R = \Sigma / /F/_{obsd.} - /F/_{calcd.} / /\Sigma / F/_{obsd.}$, for the 22 (*hk*0) reflections is 0.15, and for the 18 (0*kl*) reflections, 0.21. The probable reason for the high value of R for the (0*kl*) data is that the crystal was

TABLE II

	NEUTRON DIFFRACTION DATA					
Refin. no. ^a	Indices	jF^2 (caled.)	∑jF2 (calcd.)	jF^2 (obsd.)		
1	110	2	2	0		
2	111	1	1	0		
3	200, 002	1, 13	14	\sim_0		
4	111	480	48 0	504		
5	202	333	346	410		
$\frac{6}{2}$	112	13 J	510			
7	112	131	131	(120)		
8	020	43	43	\sim_0		
9	021, 202	132, 48				
10	113	119	642	746		
11	311	284	0	110		
12	310	59				
13	312	20	20	~ 0		
14	221, 022, 220	24, 41, 37	218	216		
15	113	87	-10	-10		
16	311	29				
17	221	15				
18	222	54	191	178		
19	313	6	, 1./1	110		
20	004	5				
21	204, 402, 400	28, 2, 81				
22	114	68				
23	023	24				
24	312	14				
25	222	34				
26	223	135				
27	114	5				
28	130	12				
29	314	12				
30	131	78				
31	131	0				
32	204, 402	82,48				
33	421, 132	0,0				
34	404	52				
35	313	4				
36	024, 223	22, 107				
37	224, 42 0	25, 29				
38	422	19				
39	115	34				
40	511	3				
41	132	111				
42	512	8				
43	510	9				
44	421	113				
45	423	0				
40	133	6				
47	331, 315	1,67				
48	913 990	112				
49 F0	33 ∪ ১০ন	71				
00 E1	004 115	30 0				
ວາ ຮຸດ	511	5 19				
02 #2	011 221 122	18				
54	994	44 6				
0-1	<i></i>	U				

^e Reflection number corresponds to line position on Fig. 1. Some reflections are too close to be resolved on Fig. 1, and have been listed together. Reflections not resolved by neutron diffraction are tied together with brackets except at angles above 40° , where nothing is well resolved. so large that omission of the absorption correction is quite serious.

Location of the Carbon Atoms.—The contribution of carbon scattering to the X-ray diffraction diagrams of ThC_2 is negligible as witnessed by the fact that no peaks due to carbon appeared on any of the projections discussed in the preceding section. With neutron diffraction, however, such is not the case.

Shull⁵ has found the coherent scattering factors for neutrons of 1.057 Å. wave length to be, for thorium, 1.01 \times 10⁻¹² cm., and for carbon, 0.64 \times 10⁻¹² cm. Since there are twice as many carbons as thoriums in the structure, the carbon coherent scattering is quite as important as the thorium scattering for neutrons of this wave length.

The neutron diffraction powder diagram, (Fig. 1), obtained by C. G. Shull, using the apparatus and method described by Wollan and Shull,⁶ was indexed on the basis of the monoclinic cell, above. There are no maxima which violate the symmetry as found by X-ray diffraction, so space groups Cc or C2/c must furnish satisfactory carbon positions. Beyond $2\theta = 40^{\circ}$, the resolution is such that no useful information could be obtained from the neutron data, though the minima occurring at 45, 50 and 55° are accounted for, in a rough way, since the densities of reflections in the minima are much less than in the adjacent regions.



Fig. 1.—Neutron diffraction pattern for ThC_2 . Lines above the curve correspond to reflection numbers as given in Table II.

Wollan and Shull have been able to determine absolute neutron intensities with their apparatus, and the absolute integrated intensities for the main neutron peaks are given, along with calculated absolute intensities, in Table II. Absolute intensities for the sample used were calculated by the equation

$$P_{hkl} = \frac{K j_{hkl} F^2_{hkl}}{\sin^2 2\theta_{hkl}}$$

where K is determined by the size and nature of sample, and the constants of the apparatus. For this case, Shull has determined K to be 0.35 \times 10^{-24} . P is in neutrons per four minutes, j is the multiplicity of the powder reflection, F is the structure factor for neutrons using the scattering factors given above, and $\sin^2 2\theta$ is the Lorentz factor for the block powder diffraction technique employed.

The resolution of the neutron diffraction data was so poor that only a trial and error determination of the carbon parameters was possible. In C2/c, only the general 8-fold set of positions is available for the 8 carbon atoms in the unit cell. If the space group is Cc, which has only the general (5) C. G. Shull, Oak Ridge National Laboratories, private communication.

(6) E. O. Wollan and C. G. Shull, Phys. Rev., 73, 830 (1948).

4-fold set of positions given earlier, the problem is one involving 6 parameters. A satisfactory structure was found in the centrosymmetric space group, C2/c.

In the trial and error determination of the carbon parameters, the thorium positions given in the preceding section were used. The general set of positions in space group C2/c is (f): $\stackrel{\sim}{\pm}(x, y, z; x, \overline{y}, z)$ $\frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} + y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ z). In this set, there is one position per octant, so only parameter values between 0 and 1/2 needed to be considered.

 $I_{(002)}$ is very weak and thus $z_{\rm C}$ is close to 0 or 1/2. $I_{(111)} > I_{(11\bar{1})}$ eliminates $z_{\rm C} \approx 1/2$, leaving $z_{\rm C} \approx 0$.

 $I_{(200)}$ is very weak and thus $x_{\rm C} \simeq 1/4$. $I_{(020)}$ is weak and thus $y_{\rm C} \simeq 0.1$ or 0.4. Since $I_{(110)}$ is very, very weak, $x_{\rm C} \leq 1/4$ if $y_{\rm C} \simeq 0.4$ or $x_{\rm C} \geq 1/4$ if $y_{\rm C} \simeq 0.1$. Using the relationships in Table III in a generative the formula of the fo eral way, the former possibility is eliminated, leaving $x_{\rm C} \ge 1/4$, $y_{\rm C} \ge 0.1$, $z_{\rm C} \ge 0$.

TABLE III

RELATIONSHIPS USED TO DETERMINE THE PLANES ENCLOS-ING THE ALLOWED REGION OF PARAMETER VALUES FOR THE CARBON ATOMS

Relationship	Points defining the plane			
$I_{112} \gg 3I_{020}$	y = 0.135			
$I_{202} \ge 2I_{112}$	(0.260, 0.135, 0.084), (0.284, 0.135,			
	0.098) (0.275, 0.125, 0.087)			
$I_{111} \ge 3.4I_{112}$	(0.284, 0.135, 0.098), (0.321, 0.135,			
	0.064), $(0.275, 0.125, 0.087)$			
$I_{221} + I_{022} + I_{220}$	(0.260, 0.135, 0.084), (0.321, 0.135,			
$\leq I_{113} + I_{311}$	0.064), (0.275, 0.125, 0.087)			

Each of the relationships in Table III defines a nearly plane surface in parameter space which divides the above region into allowed and disallowed volumes. The four planes defined in this way form an irregular triangular pyramid enclosing the allowed region of parameter values. There are no other critical intensity relationships which can be used with confidence to further limit the carbon parameters, due mainly to the poor resolution of the neutron diffraction data.



TH C2

Fig. 2 .- Structure of ThC2: dashed lines outline pseudotetragonal unit.

The carbon parameters $x_{\rm C} = 0.290$, $y_{\rm C} = 0.132$, $z_{\rm C} = 0.082$, together with $y_{\rm Th} = 0.202$, give about the optimum agreement between observed and calculated neutron diffraction intensities. The intensities calculated using these parameter values are given in Table II. It is to be noted that the calculated and observed intensities are absolute intensities, and that since K in the formula for the calculated intensities was known independently, the absolute as well as relative agreement is significant.

Though several reflections occur in several of the neutron maxima, the shape of the peak often indicates the relative intensities of reflections within one peak. Upon comparing Fig. 1 with Table II, it is seen that the agreement in this respect is also satisfactory. In making comparison, it is to be noted that defocusing broadens peaks at higher angles. Thus, $(22\overline{3})$ should be 40% broader, and not much more than half as high as (112), which makes it barely above the background level.

Discussion of the Structure.—The structure of ThC₂ is a great distortion of the tetragonal structure previously proposed. The relation between the pseudo-tetragonal cell and true cell are shown in Fig. 2. There are still definite C_2 groups in the structure, and the thorium positions would be nearly identical with those of the previously reported structure if y_{Th} were 0.25 instead of 0.20. More pronounced are the differences in the carbon positions. In Table IV, bond distances are given for the parameter values above together with those of the extremes allowed by the neutron intensities.

TABLE IV

ChC.	Bown	DISTANCES
$n \mathbf{U}_2$	BOND	DISTANCES

		-				
			Carl	on parame	etersa	
Bond	No.	I	II	III	IV	v
CC	1	1.47	1.46	1.47	1.53	1.59
Th~C A ^b	2	2.43	2.68	2.25	2.32	2.31
В	2	2.38	2.35	2.49	2.40	2.37
С	2	2.92	2.69	3.07	3.03	3.04
D	2	2.89	2.93	2.82	2.85	2.94
E	2	2.86	2.82	2.93	2.92	2.84
Th-Th	2	3.70				
	4	3.90				
	2	4.14				
	2	4.24				
	2	4.24				
	2	5.32				
۵ The ca	rbon p	oaramete	rs are			

	2	3	~
I	0.290	0.132	0.082
II	.321	.135	.064
III	.260	.135	.084
IV	.275	.125	. 087
v	.284	.135	.098

Parameter values II, III, IV and V are the extreme values of allowed parameters as determined by neutron diffraction. The letters are the same as those used in Figs. 3 and 4.

The configuration about the Th atoms (Fig. 3) is essentially octahedral in character. Two carbon atoms, from different C2 groups, are bonded to the Th by (B) bonds, and 4 C₂ groups are bonded to the Th by (A), (C), (D) and (E) bonds. The Th-C distance, B, (Table IV), for all sets of

allowable parameters and distance A for most sets,



Fig. 3.—Configuration about thorium: lettering of the bonds corresponds to that in Table IV.

is very close to the sum of the Pauling covalent, single bond radii for thorium and carbon (2.42 Å.).⁷ The C–C distance, about 1.5 Å., is close to the single bond C–C distance, and far beyond the experimental error larger than the triple bond distance, 1.2 Å., expected for an acetylene ion. Therefore, while the Th–C bonds undoubtedly possess ionic character in the Pauling sense, it seems appropriate to discuss the bonding in terms of covalent Th–C bonds.

The configuration about the C_2 groups (Fig. 4) can be described about equally well in three different ways. First, there are six thoriums about the C_2 group in a distorted ethane-like configuration. The distortion is such, however, that the thorium atoms 1, 2, 4 and 5 and the C₂ group lie almost precisely in a plane. Since the A and B bonds are the shortest Th-C bonds in the structure, the configuration is ethylene-like with thoriums 3 and 6 sitting in the π -orbitals of the C₂ group. Finally, thoriums 2 and 5 lie almost in a line with the carbons, so that one could describe the configuration as acetylenelike with thoriums in the two acetylene π -orbitals at right angles to each other. The plane formed by the D and E bonds is very closely normal to the plane formed by the A and C bonds. It seems not entirely fanciful to describe the bonding to the carbons as a resonance hybrid of these three interpretations.

Interpreting the bonding as ethylene-like, it is seen that the valence of carbon and thorium is four, since there will be 12 valence electrons per C_2 group. However, referring to Fig. 2, each thorium has four single Th-C bonds, B, and two π -bonds containing half an electron pair, each. Formal assignment of half the electron density in each bond then leads to five electrons per thorium, and a

(7) L. Pauling, THIS JOURNAL, 69, 542 (1947).



Fig. 4.—Configuration about C_2 group: lettering of the bonds corresponds to that in Table IV.

negative formal change for thorium, positive for the C_2 group. An acetylene-like interpretation demands no formal charges and leaves one electron per thorium for thorium-thorium bonds, while an ethane-like interpretation makes the Th-C bonds electron deficient if thorium and carbon are tetravalent. The structure suggested is metallic in character and suggests an unfilled valence band. It is interesting that pressed powders of ThC₂ conduct as well as pressed thorium metal powders.⁸

Each thorium is well shielded from other thorium atoms by carbon, and presumably the main cohesive forces of the carbide are due to Th-C bonds. Moreover, if the above interpretation is correct there are essentially no electrons for metal-metal bonding. We consider the fact that the C₂ group is not a C₂⁻ ion to be significant evidence that Th-C bonds must have enough covalent character to pull electrons out of the C₂ group, and to lend support to the covalent interpretation of interstitial compounds, MX,⁹ which ThC₂ resembles in many ways.

ThC₂ yields amost exclusively methane upon hydrolysis.¹⁰ This will probably be true of nearly all metallic carbides where the metal would be expected to be oxidized further by hydrogen ion. Methane is produced because it is favored thermodynamically, and may be a completely unreliable guide to the nature of the carbide.

Acknowledgment,—The authors are greatly indebted to Dr. C. G. Shull of the Oak Ridge National Laboratories who obtained the neutron diffraction data, determined the thorium scattering factor, and gave us the benefit of his advice and help in the course of the neutron diffraction investigation. We are also indebted to Mr. F. J. Modic and Dr. Premo Chiotti of the Iowa State College for aid in obtaining single crystals of ThC₂.

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Received January 13, 1951

⁽⁸⁾ P. Chiotti, private communication.

⁽⁹⁾ R. E. Rundle, Acta Cryst., 1, 180 (1948).

⁽¹⁰⁾ F. J. Modic, private communication.