

tory and curves $110^{\circ}58'$ and $112^{\circ}28'$ are poor, the tenth maximum, for example, having merged with its neighbor on the right. Our conclusion is that in the hexamethylenetetramine molecule in the gas phase the C-N bond angles are 109.5° with a limit of error of $\pm 1^{\circ}$.

The observed q_0 values for maxima and minima are indicated by vertical arrows in Fig. 1 and are listed in Table I with the ratios $q_{\text{calcd.}}/q_0$ for the finally accepted model with C-N = 1.48 Å. and tetrahedral angles. Consideration of Table I, and of similar comparisons for models with \angle C-N-C equal to $107^{\circ}58'$ and $110^{\circ}58'$, leads to the result C-N = 1.48 Å. with a limit of error of ± 0.01 Å., if (see above) \angle C-N-C = $109^{\circ}28' \pm 1^{\circ}$. Hampson and Stosick¹ also found C-N = 1.48 Å. by the correlation method, but reported C-N = 1.47 Å. (± 0.02 Å.) instead, perhaps on the basis of their imperfectly resolved radial distribution peak at 1.47 Å.

TABLE I
ELECTRON DIFFRACTION DATA FOR HEXAMETHYLENETETRAMINE

Max.	Min.	$q_0^{\dagger a}$	q_0	$q_{\text{calcd.}}/q_0$
	1		5.7	(1.070)
1		9.4	9.3	0.989
	2	13.6	12.7	0.986
2		17.8	17.9	1.005*
	3	23.2	22.3	1.020
4			26.5	1.008
	4		27.8	0.993
3		27.9	29.7	1.000
	4	33.6	33.6	1.003
4		36.5	36.2	0.985
	5	39.8	39.1	0.998
5		43.0	43.5	1.000*
	6		47.3	1.013
6		50.3	51.4	1.012
	7		53.9	1.018

7		59.0	1.000*
	8	63.0	1.011*
8			
		69.6	1.006
9			
	10	74.7	1.009
10		78.3	0.990
	11	81.6	.983
11		86.0	.991*
	12	89.6	1.003*
12		94.0	1.000
	13	97.6	0.995
13		100.7	1.001
		Average ^b	1.001
		Average deviation	0.008

^a Values of Hampson and Stosick.¹ For our best model, $q_{\text{calcd.}}/q_0^{\dagger} = 0.996$, a. d. = 0.029; if the first, second, fourth and fifth values are rejected (inner rings, rings adjacent to A), $q_{\text{calcd.}}/q_0^{\dagger} = 1.003$, a. d. = 0.016. ^b If only the six strongest, most symmetrical, and presumably most reliably measurable features represented by starred values are considered, the average is 1.001 and the average deviation is 0.005.

Acknowledgment.—We wish to express our gratitude to Professor Linus Pauling for suggesting this investigation, to Dr. R. A. Spurr and Mr. Kent Harmon for assistance in preparing the photographs and curves, and to the International Business Machines Corporation for the loan of the machines used in making the punched card calculations.

Summary

A reinvestigation of hexamethylenetetramine vapor by electron diffraction has led to results (C-N = 1.48 ± 0.01 Å. and \angle C-N-C = \angle N-C-N = $109.5 \pm 1^{\circ}$; C-H = 1.09 Å. and \angle H-C-H = $109^{\circ}28'$ assumed) in agreement with but more precise than those of the earlier investigation.¹

PASADENA, CALIFORNIA

RECEIVED JULY 29, 1946

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY No. 1082]

Anisotropic Oscillations in the Hexamethylenetetramine Crystal

BY P. A. SHAFFER, JR.

Whereas the carbon-nitrogen distance found for gas molecules of hexamethylenetetramine by the electron diffraction method,¹ 1.48 Å., agrees satisfactorily with the value predicted from the consideration of covalent radii,² previous investigations of the structure of hexamethylenetetramine crystals³ have indicated a lower value, about

(1) G. C. Hampson and A. J. Stosick, *THIS JOURNAL*, **60**, 1814 (1938); V. Schomaker and P. A. Shaffer, Jr., *ibid.*, **69**, 1555 (1947).

(2) L. Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, New York, 1940, p. 164.

(3) R. G. Dickinson and A. L. Raymond, *THIS JOURNAL*, **48**, 22 (1923); H. W. Gonell and H. Mark, *Z. physik. Chem.*, **107**, 181 (1923); R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934); R. Brill, H. G. Grimm, C. Hermann, and A. Peters, *Ann. Physik.*, **34**, 393 (1939).

1.44 Å. The work reported in this paper was carried out in order to determine whether or not the reported difference in this interatomic distance for the crystal and the gas is real. If the carbon-nitrogen distance is indeed this short in the crystal, it may be of interest in connection with the anomalously short carbon-nitrogen bond distances found in the amino acids.⁴

In the first X-ray study of the crystal structure of hexamethylenetetramine Dickinson and Raymond found the space group of the crystal to be $I43h$, with the edge of the cubic unit equal to

(4) For a review of observed carbon-nitrogen bond distances see E. W. Hughes and W. N. Lipscomb, *THIS JOURNAL*, **68**, 1970 (1946).

7.02 Å. There are two molecules in the unit, the eight nitrogen atoms being in the positions (0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) u, u, u ; \bar{u}, \bar{u}, u ; \bar{u}, u, \bar{u} ; u, \bar{u}, \bar{u} and the twelve carbon atoms in the positions (0, 0, 0; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) $v, 0, 0$; $0, v, 0$; $0, 0, v$; $\bar{v}, 0, 0$; $0, \bar{v}, 0$; $0, 0, \bar{v}$. The values of the parameters u and v reported by the four previous sets of investigators are given in Table I, together with the corresponding values of the carbon-nitrogen distance.

TABLE I

u	v	C-N	
0.120 ± 0.003	0.235 ± 0.004	1.44 ± 0.04	Dickinson and Raymond ^a
.12 ± .01	.26 ± .01	1.48 ± .08	Gonell and Mark
.12 ± .01	.23 ± .01	1.42 ± .08	Wyckoff and Corey
.1204 ± .0003	.2353 ± .0004	1.443 ± .010	Brill, <i>et al.</i>
.1220 ± .002	.2350 ± .002	1.448 ± .015	This paper

^a The probable errors assigned here are one-third of the maximum errors determined by Dickinson and Raymond by a conservative method.

Careful spectrometric measurements of the intensities of reflection from some planes of hexamethylenetetramine were made with $\text{CuK}\alpha$ radiation by Wyckoff and Corey, and another set of careful measurements was made with $\text{MoK}\alpha$ radiation by Brill, Grimm, Hermann and Peters. Wyckoff and Corey did not attempt a precise evaluation of the parameters u and v from their data; precise parameter values were, however, reported by Brill and his collaborators. In the present investigation a redetermination of the parameters u and v has been made with use of the data reported by Wyckoff and Corey and those reported by Brill and collaborators, analyzed by the method of least squares. In addition to the introduction of a temperature factor of the usual form, a special temperature factor corresponding to rotational thermal vibration of the hexamethylenetetramine molecules in the crystal has been considered. The existence of this rotational vibration is indicated by new X-ray data obtained at low temperature; it is also indicated by the ellipticity of the peaks of the Fourier projection of the crystal as reported by Brill, *et al.*⁸

The parameter values found by our least squares calculations, also given in Table I, differ slightly from those reported by Brill and collaborators, and correspond to the value 1.45 ± 0.01 Å. for the carbon-nitrogen distance in the molecules of hexamethylenetetramine in the crystalline substance.

A Low Temperature Study.—Several 30°-oscillation photographs of hexamethylenetetramine were taken with $\text{CuK}\alpha$ radiation at room temperature and at a temperature approaching that of liquid air, the axis of oscillation being parallel to the cube edge. This work was done in collaboration with Dr. Lindsay Helmholtz; the apparatus used to maintain the crystal at the lower temperature was that described by Helmholtz.⁵

(5) L. Helmholtz, *J. Chem. Phys.*, **3**, 740 (1935).

The crystal, roughly 0.3 mm. in each dimension, was lacquered to a small aluminum wire which served as a conducting support, and it was necessary to coat the crystal itself with lacquer to prevent its rapid sublimation at the low pressure used. The evacuated vessel which housed the crystal was provided with windows (of film base) through which the incident and reflected X-ray beams could pass.

The photographs do not permit intensity estimates to be made which approach the accuracy of the spectrometric determinations of the earlier papers. Direct estimation of intensities of reflection on the films yields the intensities uncorrected for extinction and perfection (probably slight in the liquid air case) of the crystal and for non-uniform absorption of the reflected beam by the lacquer and windows. The intensities of the room-temperature photographs are qualitatively in agreement with the intensities determined by use of the spectrometer. The liquid air photographs indicate the existence of a large average amplitude of thermal vibration at room temperature, the large angle reflections being much stronger at the lower temperature than at the higher one. The edge of the unit cell at the lower temperature is 6.95 Å.

A comparison of the ratios of intensities of some pairs of reflections for both temperatures was made. At liquid air temperature the reflection (640) is stronger than (730), but this relation is reversed at room temperature, despite the fact that the effect of the ordinary temperature factor would be to decrease (730) slightly more rapidly than (640) with increasing temperature. Calculated intensities based on $u = 0.119$ and $v = 0.234$ are in the order (640) > (730) at low temperature as well as room temperature, and the expected slight increases in the values of the parameters due to contraction of the cell on cooling (assuming that the molecules do not change in size) are not capable of producing the observed inversion of order.

The reflection (310) appears weaker at the lower temperature than at the higher one. This also is contrary to the usual temperature effect.

The Calculation of the Structure Amplitudes.

—A preliminary Fourier projection of hexamethylenetetramine was made in the direction parallel to a cube edge, with use of the data of Brill, *et al.* The parameter values obtained from this projection are $u = 0.119$ and $v = 0.234$. Structure amplitudes were calculated for the ($h\bar{k}0$) reflections with these parameters. The scattering factors used were those of Hartree which are tabulated in the "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Vol. 2, p. 571.⁶ For the nitrogen atoms the neutral N factors were used, and for the methylene groups the scattering factors were taken equal to those for

(6) Published by Gebrüder Borntraeger, Berlin, 1935; revised edition, reprinted by Edwards Brothers, Inc., Ann Arbor, Michigan, 1944.

carbon plus the difference between the factors for the oxide ion and for neutral oxygen. Table II contains the structure amplitudes observed by Brill, Grimm, Hermann and Peters, F_B (obs.), those observed by Wyckoff and Corey, F_W (obs.), the calculated amplitudes of Wyckoff and Corey, F_W (calcd.), and those calculated using the above parameters, F_1 . The expression for the structure amplitudes of the (h k 0) planes is

$$F = \exp \left\{ -B \left(\frac{\sin^2 \theta}{\lambda^2} \right) \right\} \{ 4f_{\text{CH}_2} (\cos 2\pi hv + \cos 2\pi kv + 1) + 8f_N \cos 2\pi hu \cos 2\pi ku \} \text{ for } h + k = 2n \quad (1)$$

$$F = 0 \text{ for } h + k = 2n + 1$$

where f_{CH_2} is the scattering factor for the methylene group, etc., and the factor $\exp(-B(\sin^2\theta/\lambda^2))$ is a temperature factor corresponding to isotropic oscillations of the atoms. In the calculations which are given under F_1 in Table II, B is 4.5. Wyckoff and Corey used no explicit temperature factor in their calculations.

TABLE II

$hk0$	F_B (obs.)	F_W (obs.)	F_W (calcd.)	F_1	F_2	F_3
110	52.8	52.6	52.8	48.7	47.3	44.1
200	20.4	17.6	22.0	18.5	18.0	15.9
220	14.5	16.6	-12.9	-10.0	-12.1	-12.2
310	3.19	5.3	-6.9	-3.7	-4.2	-4.6
400	0	0	-4.6	2.2	2.5	2.3
330	10.6	14.6	12.8	8.7	7.7	8.6
420	5.84	8.9	4.6	4.3	4.9	5.4
510	1.20	0	-2.5	0.7	0.5	0.2
440	21.1	23.1	26.0	20.2	22.2	21.0
530	9.16	13.0	11.5	8.6	10.0	9.2
600	0	0	2.0	2.4	0.4	0.1
620	3.10	4.9	-3.0	-2.6	-3.4	-3.1
550	7.04	10.4	10.9	7.9	8.6	7.7
710	2.76	3.7	4.7	2.8	2.0	2.3
640	2.08	2.4	4.3	3.4	3.0	1.8
730	2.31	3.5	-2.4	-1.1	-1.8	-1.8
800	7.58			7.1	8.7	7.8
820	2.39			1.2	2.4	2.1
660	3.35			-0.7	-2.6	-2.7
750	1.84			0	-1.3	-1.3
840	0			0.7	0.8	0.6
910	3.57			3.0	4.4	3.3
930	0			0.2	0.5	0.3
770	0			0.2	-0.8	-0.3
10.0.0	0			1.3	0.7	0
860	0			0.2	0.4	0.6
10.2.0	1.34			-0.2	-1.1	-1.1
950	0			0.3	0.6	0.6
10.4.0	0			0.2	-0.5	-0.3
11.1.0	1.06			-0.1	-1.2	-0.7
880	2.28			1.3	1.9	1.6
				4.5	2.25	2.4
				0	2.5	2.8
				0.119	.119	.122
				.234	.234	.235
						B
						b
						u
						v

The agreement of F_1 with the observed F 's leaves much to be desired. In order to obtain the best possible fit, least-squares calculations were carried out with increments of the parameters as the variables in the manner described by Hughes⁷; in addition, the scale factors which need to be applied to the observed amplitudes were adjusted as a part of the least squares treatment. The least squares normal equations were obtained with the

(7) E. W. Hughes. *THIS JOURNAL*, **63**, 1737 (1941).

use of International Business Machines Corporation machines in about one hour.⁸ Although the least square computations result in improved agreement of the calculated and experimental F 's as indicated by a several-fold decrease in the sum of the squares of the residuals in all cases, somewhat different parameters arise from the two sets of data. The agreement between the two sets of results is improved by the omission of the first few reflections to avoid uncertainties due to extinction. However, there remain important discrepancies (1) the temperature inversion of the intensity relation between (730) and (640), (2) the opposite of the expected effect of temperature on (310), and (3) the disagreement of the calculated and observed F 's for (10.2.0) and (11.1.0).

The Effect of Angular Oscillation of the Molecule

In an effort to explain the temperature effects noted in the preceding paragraphs as well as to obtain a better over-all agreement of calculated and observed structure amplitudes, the roughly spherical molecule of hexamethylenetetramine was assumed to undergo angularly symmetric oscillations about its center of gravity in addition to the isotropic vibration of each atom about its assumed rest point. For convenience, these two effects were treated separately, the isotropic part of the temperature factor appearing as $\exp(-B(\sin^2\theta/\lambda^2))$ as before; B , therefore, is in units of \AA^2 . The introduction of a corresponding constant b which is related to the degree of anisotropy due to angular oscillation is exemplified by the treatment for the methylene group assumed to be at the point (0,0, v) on the z axis. The time average distribution of this group is taken to be (neglecting the isotropic factor)

$$p(x,y) = \frac{4\pi a_0^2}{b} \exp \left\{ -\frac{4\pi^2 a_0^2}{b} (x^2 + y^2) \right\} \quad (2)$$

where x and y are in fractions of the unit cube edge, a_0 . The component of the structure amplitude which is due to this atom is therefore

$$F_{\text{CH}_2}(0,0,v) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \{ 2\pi i(hx + ky + lz) \} p(x,y) dx dy = f_{\text{CH}_2} \exp \{ 2\pi ilz \} \exp \left\{ -\frac{b}{4a_0^2} (h^2 + k^2) \right\} \quad (3)$$

Summed over the methylene groups for the (h k 0) planes, the final result is

$$F_{\text{CH}_2} = 4f_{\text{CH}_2} \left\{ \cos 2\pi hv \cdot \exp \left(-\frac{bk^2}{4a_0^2} \right) + \cos 2\pi kv \cdot \exp \left(-\frac{bh^2}{4a_0^2} \right) + \exp \left(-\frac{bh^2 + bk^2}{4a_0^2} \right) \right\}$$

$$\text{for } h + k = 2n \quad (4)$$

$$F_{\text{CH}_2} = 0 \text{ for } h + k = 2n + 1$$

In a similar way the total contribution of the nitrogen atoms is found to be

(8) This procedure is described by P. A. Shaffer, Jr., Verner Schomaker and Linus Pauling, *J. Chem. Phys.*, **14**, 657 (1946).

$$F_N = 8f_N \exp \left\{ -\frac{b}{6\sigma_0^2} (h^2 + k^2) \right\} \left\{ \cosh \frac{bkk}{6\sigma_0^2} \cos 2\pi hu \right. \\ \left. \cos 2\pi kv - \sinh \frac{bkk}{6\sigma_0^2} \sin 2\pi hu \sin 2\pi kv \right\} \\ \text{for } h + k = 2n \quad (5)$$

$$F_N = 0 \text{ for } h + k = 2n + 1$$

The complete structure amplitude is now

$$F = \exp \left(-B \frac{\sin^2 \theta}{\lambda^2} \right) (F_{\text{CH}_2} + F_N) \quad (6)$$

The half-widths of the distribution (assumed equal for CH₂ and N) are

$$w_{1/2}(\text{max.}) = 0.1325 \sqrt{B + b}, w_{1/2}(\text{min.}) = 0.1325 \sqrt{B} \quad (7)$$

It is to be noted that the atoms are assumed to vibrate with random phases with respect to one another. This is certainly not true, but the calculations involving the phases are more difficult and the improvement in the representation is not expected to warrant the greater work.

The structure amplitudes were calculated with the new equation with $u = 0.119$, $v = 0.234$, $b = 2.5$ and 4.5 , and $B = 0$. Both sets of F 's showed improvement over those calculated with $b = 0$. For comparison, several sets of calculations are tabulated in Table III for pairs of reflections in which the temperature effect is most noticeable. The amplitudes calculated with $B = 2.25$ and $b = 2.5$ are listed in Table II under F_2 . It is seen that the inclusion of the anisotropic temperature effect improves the agreement considerably.

TABLE III

hkl	$F_B(\text{obs.})$	$F(b = 0)$	$F(b = 2.5)$	$F(b = 4.5)$
310	Stronger at room temperature	4.7	4.7	5.8
640	2.08	11.1	5.5	3.0
730	2.31	4.0	3.5	3.1
860	0	2.1	1.4	0.2
10.2.0	1.34	2.5	3.5	3.3
950	0	3.3	2.0	1.6
10.4.0	0	3.1	1.7	2.2
11.1.0	1.06	2.1	4.8	4.9
880	2.28	23.3	8.3	4.2

To obtain the optimum values of u , v , B and b , a second set of least-squares calculations were made for both $F_B(\text{obs.})$ and $F_W(\text{obs.})$. In this case nearly the same structure parameters result from the use of both the Brill data and the Wyckoff and Corey data. The averages of the parameters derived from these two sets of data are $u = 0.122$, $v = 0.235$, $B = 2.4$ and $b = 2.8$; the structure amplitudes computed for these values of the parameters are listed under F_2 in Table II. Although no probable errors based on the residuals have been computed, the sensitivity of the results to changes in the selection of the data lead to estimated limits of error of about ± 0.002 for the atom positions and roughly ± 0.2 for the temperature factor parameters. On the basis of this con-

clusion, it seems unlikely that the limits of error assigned to their results by Brill, *et al.*, indicate the extent of the uncertainties involved.

Discussion of the Structure

The C-N distance in the hexamethylenetetramine molecule in the crystal is 1.448 Å. The C-N-C angle is 107°19', and the closest approach of the carbon atoms is 2.33 Å. The longer C-C distance, that between two carbon atoms in the same molecule and on the same cube edge, is 3.30 Å. The N-N distance is 2.42 Å., the N-C-N angle being 113°30'. The non-adjacent C-N distance is 2.78 Å. Each molecule is surrounded by 8 nearest neighbors at 6.08 Å. (along the body diagonals) and by 6 at 7.02 Å. (along the cube edges).

A Fourier projection of the electron density distribution in the crystal was made parallel to a cube edge, using the data of Brill, Grimm, Hermann and Peters and the signs given by column F_2 in Table II. The parameters obtained from the Fourier projection, $u = 0.120$ and $v = 0.234$, are each less than the values which resulted from the least-squares treatment. This may be attributed in part to the effect of the foot of the large peak at the origin in raising the inside of adjacent peaks and thus drawing the peaks in toward the larger one, and a similar effect of the nitrogen peaks in drawing in the outer methylene peaks.

Brill, Grimm, Hermann and Peters have drawn attention to the distorted shape of the peaks, in their Fourier projection, which they attributed to a rotational oscillation of the molecule. The amplitude of this oscillation is given by the constants B and b . The root-mean-square amplitude of oscillation of each of the atoms along the radius vector connecting it with the molecular center of gravity is about 0.18 Å. The root-mean-square amplitude in a direction normal to the radius vector is about 0.26 Å.

Each molecule is held by twelve weak hydrogen bonds from its carbon atoms to the nearest nitrogen atoms of four adjacent molecules and another twelve from its nitrogen atoms to adjacent carbons. Each nitrogen atom is thus connected by hydrogen bonds to three carbon atoms and each carbon atom is hydrogen-bonded to two nitrogen atoms. The bonding takes place (on the average) parallel to the body diagonal of the cubic unit, and the bonds are 3.88 Å. in length, and form an angle of 20° with the body diagonal.

The formation of weak hydrogen bonds between the methylene carbon atoms and the nearest nitrogen atom in an adjacent molecule must be assumed to account for the stability of the crystal, which has too small an amplitude of isotropic thermal oscillation for van der Waals binding.

The decrease of the C-N-C bond angle from 109°28' to 107°19' may be due to the three hydrogen bonds, which pull the nitrogen atom away

from the center of the molecule along the body diagonal. The same effect would not be realized with the carbon atoms because the two hydrogen bonds connecting with each carbon atom make an angle of $150^{\circ}3'$ with one another and the two tensions cancel for the most part.

The existence of the hydrogen bonds between adjacent molecules, however, while expected to reduce the possibility of isotropic thermal vibration, does not greatly interfere with rotational vibrations of the molecule. Each nitrogen is at the top of a triangular pyramid whose base has a carbon atom of each vertex. The hydrogen bonds form the three near-vertical edges of this figure. Displacement of the nitrogen 0.26 \AA. in any direction parallel to the base may vary a hydrogen bond length by not more than 0.11 \AA. , and leaves the average virtually unchanged.

Acknowledgment.—I wish to express my gratitude to Professor Linus Pauling for suggesting this work to me and for the many helpful suggestions which he made during its course, and to Professor Verner Schomaker for valuable discussions. I am indebted to my wife for assistance

with the calculations, to Mr. Kent Harmon for preparing the Fourier projection, and to Dr. Lindsay Helmholtz for help with the low-temperature photographs.

Summary

A comparison of X-ray data obtained at low temperature with those obtained at room temperature indicates the existence of rotational thermal vibrations in the hexamethylenetetramine crystal. Structure amplitudes calculated on the basis of assumed rotational vibrations are in closer agreement with the observed amplitudes for room temperature than are those calculated without the use of a rotational temperature factor. A slightly altered structure which provides a better fit than any other structure considered is derived by the method of least squares. The bond angles and bond distances are $C-N = 1.45 \pm 0.01 \text{ \AA.}$; $C-N-C = 107^{\circ}$; $N-C-N = 113^{\circ}30'$. The carbon-nitrogen bond distance is about 0.03 \AA. less in the crystal than in the gas.

PASADENA, CALIFORNIA

RECEIVED⁹ MARCH 1, 1947

(9) Original manuscript received July 29, 1946.

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1087]

The Crystal Structures of Trimethylplatinum Chloride and Tetramethylplatinum

BY R. E. RUNDLE¹ AND J. H. STURDIVANT

All reported structures of quadrivalent platinum compounds have involved octahedral coordination about platinum. Presumably, however, quadrivalent platinum is capable of forming d^2sp tetrahedral bonds, and the platinum alkyls, tetramethylplatinum, hexamethyldiplatinum, trimethylplatinum chloride, etc., were expected to have this configuration.² Cox and Webster³ determined the correct unit cell with $a = 10.52 \text{ \AA.}$ for trimethylplatinum chloride from powder diagrams, but no real attempt was made to examine the structure. Since no structures involving d^2sp tetrahedral bonding have been verified, it seemed important to investigate the structures of some of the above-named compounds.

Experimental

Preparation of the Compounds.—Trimethylplatinum chloride was prepared by the action of platinum tetrachloride on methyl Grignard reagent as described by Pope and Peachey,⁴ except that the platinum tetrachloride was made according to the directions of Kharasch and Ash-

ford,⁵ and was added to the Grignard reagent as the dry powder as recommended to us by Professor Gilman. The material had the properties described by Pope and Peachey⁴ for trimethylplatinum chloride, and X-ray powder lines produced by it agreed with the measurements of Cox and Webster.³

Tetramethylplatinum⁶ was furnished us by Professor Gilman. Unlike other compounds of the type Me_4M it is a crystalline material. It is likewise less soluble in organic solvents than are other compounds of this formula.

Crystal System and Unit Cells.—Both trimethylplatinum chloride and tetramethylplatinum crystallize from benzene in anisotropic plates which quickly lose solvent of crystallization to form isotropic powders. From aliphatic hydrocarbons and the ethers they crystallize as rhombic dodecahedra of the cubic system. This habit was confirmed by the optical goniometry of several crystals of each compound. When heated the crystals decompose without melting.

By the Laue method two, three, and four-fold axes were found for both crystals in positions corresponding to the goniometry, and O_h-m3m was

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(2) Linus Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, New York, 1944, p. 102.

(3) E. G. Cox and K. C. Webster, *Z. Krist.*, **90**, 561 (1935).

(4) W. J. Pope and S. J. Peachey, *J. Chem. Soc.*, **95**, 571 (1909).

(5) M. S. Kharasch and T. A. Ashford, *THIS JOURNAL*, **56**, 1738 (1936).

(6) Henry Gilman and M. Lichtenwalter, *THIS JOURNAL*, **60**, 3088 (1938).