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°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 Å. in any direction parallel to the base may vary a hydrogen bond length by not more than 0.11 Å., 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 Helmholz 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 ± 0.01 Å.; C–N–C = 107°; N–C–N = 113°30′. The carbon–nitrogen bond distance is about 0.03 Å. less in the crystal than in the gas.

PASADENA, CALIFORNIA RECEIVED[9] 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. RUNDLE[1] AND J. H. STURDIVANT

All reported structures of quadrivalent platinum compounds have involved octahedral coördination 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 Webster[3] determined the correct unit cell with a = 10.52 Å. 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 Ashford,[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 Peachey[4] for trimethylplatinum chloride, and X-ray powder lines produced by it agreed with the measurements of Cox and Webster.[3]

Tetramethylplatinum[6] 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

---

[1] Present address: Department of Chemistry. Iowa State College. Ames, Iowa.

[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. **58**, 1733 (1936).

[6] Henry Gilman and M. Lichtenwalter. THIS JOURNAL. **60**, 3085 (1938).

established as the Laue symmetry. With the radiation from a copper target filtered through nickel and a camera of 5-cm. radius intense exposures (800 to 1000 milliampere hours at 38 kv. peak) were made with the crystals rotating about two and three-fold axes. These could be indexed on the basis of body-centered cubic units, with a = 10.55 Å. for trimethylplatinum chloride, and a = 10.145 Å. for tetramethylplatinum. Powder diagrams also were indexed by use of these units and in the case of tetramethylplatinum the unit was tested further by the indexing of Laue diagrams.

The density of tetramethylplatinum, as determined by the flotation of crystals in solutions of methylene iodide and methyl iodide, is 3.16 g./cc. The density calculated for eight Me_4Pt molecules per unit cell is 3.23 g./cc. The density of trimethylplatinum chloride has been found[8] to be 3.1 g./cc.; hence it contains eight Me_3PtCl molecules per unit cell.

Space Group Discussion.—Though the X-ray data indicate the Laue symmetry O_h and a body-centered lattice, it is questionable whether this evidence can be considered binding for the methyl groups, whose scattering power is relatively low. We shall, however, accept it for the arrangement of the platinum atoms in both crystals, and for the chlorine atoms in trimethylplatinum chloride. Possible space groups for these atoms are then[7] T_d^3–$I\bar{4}3m$, O^5–$I43$, O^8–$I4_13$, and O_h^9–$Im3m$. The positions[7] for eight platinum atoms, when the origin is chosen suitably in each case, are the following:

$(000;\ {}^1/_2\,{}^1/_2\,{}^1/_2)\ +$

(α) $000;\ 0\,{}^1/_2\,{}^1/_2;\ {}^1/_2\,0\,{}^1/_2;\ {}^1/_2\,{}^1/_2\,0.$

(β) ${}^1/_8\,{}^1/_8\,{}^1/_8;\ {}^5/_8\,{}^3/_8\,{}^7/_8;\ {}^7/_8\,{}^5/_8\,{}^3/_8;\ {}^3/_8\,{}^7/_8\,{}^5/_8.$

(γ) ${}^3/_8\,{}^3/_8\,{}^3/_8;\ {}^7/_8\,{}^1/_8\,{}^5/_8;\ {}^5/_8\,{}^7/_8\,{}^1/_8;\ {}^1/_8\,{}^5/_8\,{}^7/_8.$

(δ) $u\,u\,u;\ u\,\bar{u}\,\bar{u};\ \bar{u}\,u\,\bar{u};\ \bar{u}\,\bar{u}\,u.$

Atoms occupying the set of positions (α) make no contribution to the intensity of maxima with h_1, h_2, or h_3 odd. Many reflections of the form ($2n + 1$, $2n + 1$, $2n$) are so intense on rotation diagrams from both compounds that their reflections must necessarily involve a large platinum contribution. The positions (α) are therefore eliminated for platinum. The sets (β) and (γ) are enantiomorphs, and intensities calculated for an array of platinum atoms alone in either of these sets are in rough agreement with those observed for both compounds. If the platinum atoms are in (δ) the parameter u is limited to the neighborhood of $\pm{}^1/_8$ or $\pm{}^3/_8$; these values of u produce congruent or enantiomorphic motifs; their intensities are identical with those from (β) or (γ). Then (β), (γ), and (δ) offer possible platinum positions.

If the platinum atoms were in (β) or (γ), the crystals of trimethylplatinum chloride and tetramethylplatinum could be optically active; actually an examination failed to reveal optical activity. The negative result of this sensitive test suggests strongly that the positions (β) and (γ) should be considered no further. Fortunately, for both crystals it is possible to eliminate the positions (β) and (γ) on other evidence as well.

Platinum atoms in positions (β) or (γ) contribute nothing to reflections of the forms ($4n$, $4n$, $4n + 2$) and ($4n + 2$, $4n + 2$, $4n$). These reflections appear to be absent for trimethylplatinum chloride, but for large values of the Bragg angle several such reflections were observed from tetramethylplatinum. The intensities of these reflections are too great to be explained on the basis of the scattering of the carbon atoms alone; hence the positions (β) and (γ) are eliminated for the platinum atoms in tetramethylplatinum. For this compound the platinum atoms must be in (δ) with u near, but not equal to, ${}^1/_8$ or ${}^3/_8$.

The positions (β) and (γ) can be eliminated for the platinum atoms in trimethylplatinum chloride only by considering the chlorine positions along with the platinum positions. The positions available for the eight chlorine atoms are again (α), (β), (γ), and (δ). With the chlorine atoms in (α) and the platinum atoms in (β), (γ), or (δ), it is easily shown that reflections of the form ($4n + 2$, $4n + 2$, $4n + 2$) should be stronger than reflections ($4n$, $4n$, $4n$) with n odd. In every case where such reflections occur in the same vicinity the opposite is true. The difference is too great to be accounted for by carbon contributions, and the set (α) is thus eliminated for the chlorine atoms.

With the platinum atoms in (β) the only remaining set of positions for the chlorine atoms consistent with the cubic symmetry is (γ). If we consider reflections of the type ($2n + 1$, $2n' + 1$, $2n''$) we find that for the above structure the structure factors fall into two groups. For n, n', n'' even, for n, n'' even, n' odd, and for n, n' odd, n'' even, $F = \pm 4i(f_{Pt} - f_{Cl})$. For n, n' even, n'' odd, for n, n'' odd, n' even, and for n, n', n'' odd, $F = \pm 4(f_{Pt} + f_{Cl})$. Examination of a large number of reflections of the above type revealed that reflections of the first group were more intense than those of the second whenever comparisons were possible. The structure under consideration is, therefore, eliminated. The enantiomorphic structure with the chlorine atoms in (β) and the platinum atoms in (γ) need not be considered. The positions for both platinum atoms and chlorine atoms must be (δ). As will be seen, these positions provide a satisfactory structure.

Of the space groups previously listed, only T_d^3–$I\bar{4}3m$ is permitted. It is true, however, that the space groups T_d^1–$P\bar{4}3m$ and T_d^4–$P\bar{4}3n$ furnish the positions chosen for the platinum and chlorine atoms. If the methyl groups are not arranged on a body-centered lattice one of these space groups must be chosen for the structure. For the space group T_d^1–$P\bar{4}3m$, the point symmetry of the platinum and chlorine atoms is C_{3v}–

---

(7) "International Tables for the Determination of Crystal Structures," Gebrüder Borntraeger, Berlin, 1935, Vol. I.

$3m$, as it is for T_d^3–$I\bar{4}3m$, but each set of positions is divided into two non-equivalent sets of four positions. No arrangement of the methyls seems to call for non-equivalence of the eight platinum or chlorine atoms. In T_d^4 the eight positions in each set are equivalent but have the point symmetry $C_3 - 3$. Again it seems unnecessary to consider for the methyls distorted configurations which would lower the point symmetry of the platinum and chlorine atoms. For these reasons, the space group T_d^3–$I\bar{4}3m$ was chosen for both crystals; that it provides satisfactory structures is added justification for this choice.

Determination of the Parameters for Trimethylplatinum Chloride.—With the platinum atoms in (δ) with $u_{\mathrm{Pt}} = {}^3/_8$ both rough intensity considerations and steric factors limit the chlorine parameter to the neighborhood of ${}^1/_8$. For a more accurate determination of the platinum and chlorine parameters, it was necessary to obtain good intensity data, corrected accurately for the high absorption of platinum. For this purpose a small crystal was attached by shellac to a glass fiber, with the fiber axis parallel to a two-fold axis of the crystal. The crystal was well centered on the fiber and the shellac was baked until firm. The crystal was then ground to a cylinder on a milling machine using a rotating ground glass plate as the grinding surface. Under the microscope the crystal appeared to be a smooth cylinder 0.14 mm. long, 0.1 mm. in diameter. This crystal was used in preparing intense rotation diagrams with CuKα radiation filtered through nickel foil 70 μ thick; at 38 kv. p. exposures ran to 975 milliampere hours. The interference maxima produced very symmetrical, clean spots on the photographic film. Relative intensities were visually estimated by the multiple film technique.[8] The absorption correction was made according to Claassen[9]; the linear absorption coefficient equals 471 for trimethylplatinum chloride and $\lambda = 1.54$ Å. The intensity data were analyzed in the steps outlined in the following paragraphs.

The reflection (929) is easily visible, but (2.12.2) was not observed. This requires $u_{\mathrm{Pt}} < 0.385$ regardless of the chlorine and carbon parameters. That (929) is but a fourth as intense as (6.10.6) requires $u_{\mathrm{Pt}} > 0.370$, again regardless of the chlorine and carbon contributions to these reflections. If, in accordance with our earlier observation, we restrict u_{Cl} to 0.125 ± 0.025, and then add the most unfavorable possible combination of contributions from chlorine and carbon atoms to the variable contribution from platinum atoms, we obtain the relative intensities for (929), (2.12.2), and (6.10.6) which are plotted in Fig. 1 as functions of u_{Pt}. The most unfavorable conditions differ widely, as shown by the break in the (929) curve. Any reasonable compromise leads to $u_{\mathrm{Pt}} = 0.375 \pm 0.002$.

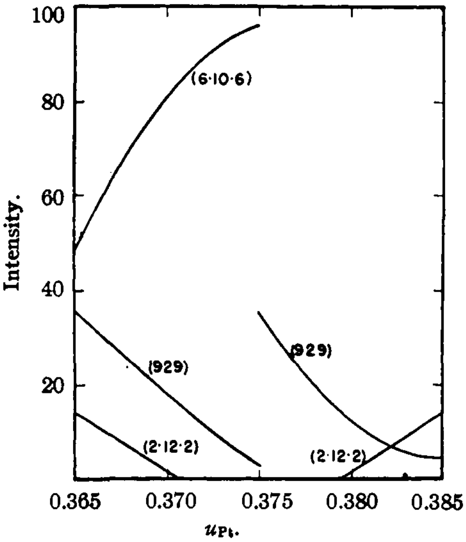

Fig. 1.—Determination of the platinum parameter in trimethylplatinum chloride.

The reflections ($4n$, $4n$, $4n$) are more intense than reflections ($4n + 2$, $4n + 2$, $4n + 2$). The contributions of the platinum atoms to the structure factors of these reflections are very closely equal in magnitude even for small variations in the platinum parameter; hence these reflections are most useful in determining the chlorine parameter. Thus the observation $(\bar{4}.12.\bar{4}) > (\bar{6}.10.\bar{6})$ requires that $0.100 < u_{\mathrm{Cl}} < 0.150$ regardless of the carbon contribution.

Further refinement of the chlorine parameter demands that some account be taken of the positions of the carbon atoms. These cannot be determined from X-ray evidence because of the low scattering power of carbon relative to platinum; but from the structure as determined thus far the rough positions of the carbon atoms become apparent. Thus from the positions of the platinum and chlorine atoms it is obvious that trimethylplatinum chloride is a tetramer (Figs. 2 and 3), with each platinum atom bonded to three chlorines, each chlorine to three platinums. Four chlorine atoms together with four platinum atoms form a rough cube, the platinum atoms forming one tetrahedron, the chlorine atoms its negative. Chemically, we should expect three methyls to be bonded to each platinum atom. This arrangement is achieved by filling out the octahedron about platinum, giving platinum the same type of coördination that it shows in all other quadrivalent compounds. The carbon atoms can then be placed in the positions[7] 24 (g) of the space group T_d^3–$I\bar{4}3m$. If the carbon–platinum distance is assumed to equal the sum of the covalent radii (2.08 Å.),[10] then $x_{\mathrm{C}} \cong 0.375$ and $z_{\mathrm{C}} \cong 0.18$. To permit refinement of the chlorine parameters these carbon parameters need be only exact enough to yield approximate values of the contri-

---

(8) J. J. de Lange, J. Monteath Robertson and I. Woodward, *Proc. Roy. Soc.* (*London*), **A171**, 404 (1939).

(9) *Cf.* (7), Vol. II, pp. 583–585.

(10) Linus Pauling, ref. 2, pp. 164 and 182.

butions of the carbon atoms to the various reflections.

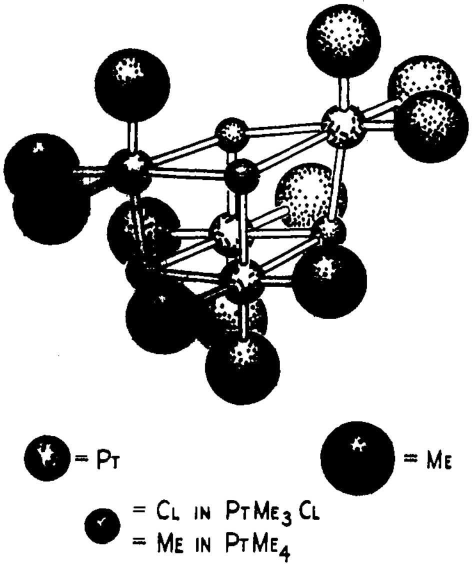

Fig. 2.—The tetramer which occurs in crystalline trimethylplatinum chloride and tetramethylplatinum.

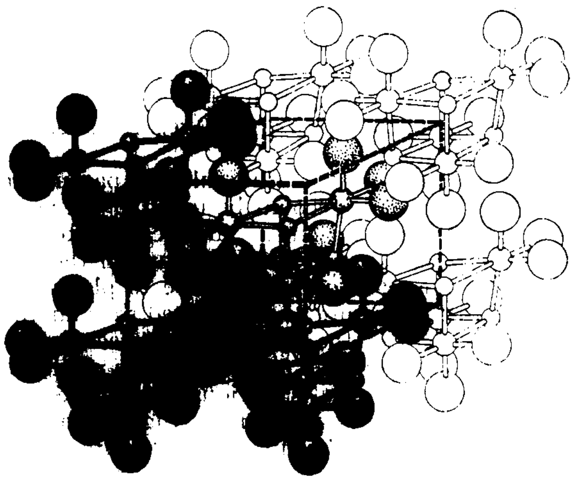

Fig. 3.—The cubic unit of structure of crystalline trimethylplatinum chloride and tetramethylplatinum; the tetramer shown in Fig. 2 is repeated by parallel displacement at the points of a body-centered cubic lattice.

If we now reconsider the chlorine parameter we find that $(\bar{4}.12.\bar{4}) > (\bar{6}.10.\bar{6})$ requires $0.105 < u_{Cl} < 0.145$. The observation $(\bar{5}.10.\bar{5}) > (\bar{1}.12.\bar{1})$ requires that $u_{Cl} \cong 0.11$ (Fig. 4). The best value for the chlorine parameter seems to be $u_{Cl} = 0.11 \pm 0.01$. To refine the parameter further seems pointless in view of the uncertainty in the carbon parameters.

Table I lists experimental and calculated intensities for the reflections in the [101] zone. The experimental data were derived as described above from rotation photographs prepared with a cylindrical crystal. The symbols in the table have the following significance

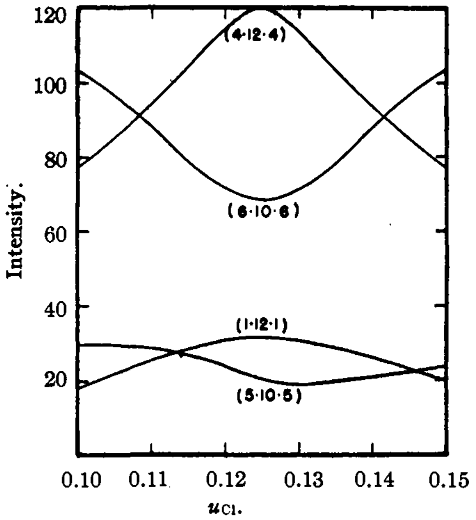

Fig. 4.—Determination of the chlorine parameter in trimethylplatinum chloride.

$$I'_{exp.} = I_{exp.} KA (\sin 2\vartheta)/(1 + \cos^2 2\vartheta)\, e^{-k\Sigma h^2}$$

where $I_{exp.}$ is the experimentally observed intensity of reflection, K is a convenient constant, A is the absorption correction, and k, in the exponent of the temperature-correction factor, was given the value 0.022; and

$$I'_{calcd.} = K'FF^*J$$

where K' is a convenient constant, F is the structure amplitude and F^* its complex conjugate, and J is the multiplicity factor. The agreement between observed and calculated intensities is seen to be satisfactory.

Determination of the Parameters for Tetramethylplatinum.—For this compound the platinum parameter alone could be determined from X-ray data. It was hoped that some direct information could be obtained concerning the carbon positions, but this hope proved vain, in part because of the difficulty in making reliable absorption corrections. Attempts to prepare cylindrical crystals failed due to the instability and insolubility of the compound. Since, however, tetramethylplatinum crystallizes in the same form as trimethylplatinum chloride and has the same absorption coefficient, approximate corrections could be made by comparing reflections from trimethylplatinum chloride dodecahedra with reflections from the cylindrical crystal of this compound. The observed correction factor for each plane was used to correct the intensities of corresponding reflections from dodecahedral crystals of tetramethylplatinum. Except for a few planes noted in Table II the corrections were small, and this method appears to be satisfactory.

Reflections of the forms ($4n$, $4n$, $4n + 2$) and ($4n + 2$, $4n + 2$, $4n$) are weak, but are definitely present in many cases. Their presence cannot be

TABLE I

TRIMETHYLPLATINUM CHLORIDE: INTENSITIES OF EQUATORIAL REFLECTIONS ON [101] ROTATION PHOTOGRAPHS

		I'		
$h_1h_2h_3$	$I_{exp.}$	Exp.	Calcd.	Calcd.[a]
$\bar{1}0\bar{1}$	3400	151	180	180
020	0	0	0	0
$\bar{1}2\bar{1}$	2450	196	172	138
$\bar{2}0\bar{2}$	0	0	0	0
$\bar{2}2\bar{2}$	2125	254	300	445
040	3730	546	540	435
$\bar{3}0\bar{3}$	1800	290	75	91
$\bar{1}4\bar{1}$			208	215
$\bar{3}2\bar{3}$	285	55	62	78
$\bar{2}4\bar{2}$	0	0	0	0
$\bar{4}0\bar{4}$	1300	366	388	344
$\bar{3}4\bar{3}$	425	127	116	144
$\bar{4}2\bar{4}$	0	0	2	2
060			1	2
$\bar{1}6\bar{1}$	330	112	98	95
$\bar{2}6\bar{2}$	650	267	300	330
$\bar{4}4\bar{4}$	1300	600	575	550
$\bar{5}0\bar{5}$	170	84	108	90
$\bar{5}2\bar{5}$	275	150	104	100
$\bar{3}6\bar{3}$			63	62
080	350	248	264	246
$\bar{1}8\bar{1}$	320	238	109	125
$\bar{5}4\bar{5}$			190	155
$\bar{4}6\bar{4}$	0	0	1	1
$\bar{6}0\bar{6}$	0	0	0	0
$\bar{2}8\bar{2}$			1	1
$\bar{6}2\bar{6}$	295	275	287	280
$\bar{3}8\bar{3}$	95	100	75	77
$\bar{5}6\bar{5}$	105	116	95	80
$\bar{6}4\bar{6}$	0	0	1	1
$\bar{4}8\bar{4}$	320	430	384	370
$\bar{7}0\bar{7}$	22	29	44	40
0.10.0	0	0	2	2
$\bar{7}2\bar{7}$	55	80	21	35
$\bar{1}.10.\bar{1}$			85	64
$\bar{2}.10.\bar{2}$	335	525	232	240
$\bar{6}6\bar{6}$			270	230
$\bar{7}4\bar{7}$	115	192	77	60
$\bar{5}8\bar{5}$			120	115
$\bar{3}.10.\bar{3}$	35	61	51	50
$\bar{8}0\bar{8}$	80	150	160	165
$\bar{8}2\bar{8}$	0	0	1	1
$\bar{4}.10.\bar{4}$			2	2
$\bar{7}6\bar{7}$	15	27	24	30
$\bar{6}8\bar{6}$	0	0	1	1
$\bar{8}4\bar{8}$	250	480	270	300
0.12.0			160	145
$\bar{1}.12.\bar{1}$	35	67	65	74
$\bar{5}.10.\bar{5}$	45	87	74	64
$\bar{2}.12.\bar{2}$	0	0	8	8
$\bar{3}.12.\bar{3}$	80	150	48	53
$\bar{7}8\bar{7}$			54	58
$\bar{9}0\bar{9}$			65	40
$\bar{9}2\bar{9}$	25	44	45	56
$\bar{6}.10.\bar{6}$	125	205	214	180
$\bar{4}.12.\bar{4}$	175	248	230	235

[a] Calculated with neglect of the carbon scattering.

attributed to scattering by carbon atoms, but these reflections are particularly sensitive to the platinum parameter. They require that $u_{Pt} = 0.375 \pm 0.006$; otherwise their calculated intensities become comparable to those of other reflections, which is contrary to observation. Reflection (707) is, however, very weak, even weaker than (0.10.0), but would become enormous if u_{Pt} were less than 0.375. The observed inequality, (1.12.1) > (5.10.5), also requires $u_{Pt} > 0.375$ (Fig. 5). The best agreement is obtained if $u_{Pt} = 0.380 \pm 0.002$. For a comparison of observed and calculated intensities see Table II. The significance of $I'_{exp.}$ is as defined above for Table I, save that the value of k used for tetramethylplatinum is 0.0083. The carbon atoms of the methyl groups which in tetramethylplatinum replace the chlorine atoms of trimethylplatinum chloride were assigned the parameter $u_{C_I} = 0.11$. The carbon atoms of the remaining methyl groups were put into positions analogous to those occupied in trimethylplatinum chloride, with assigned parameters $x_{C_{II}} = 0.375$, $z_{C_{II}} = 0.18$.

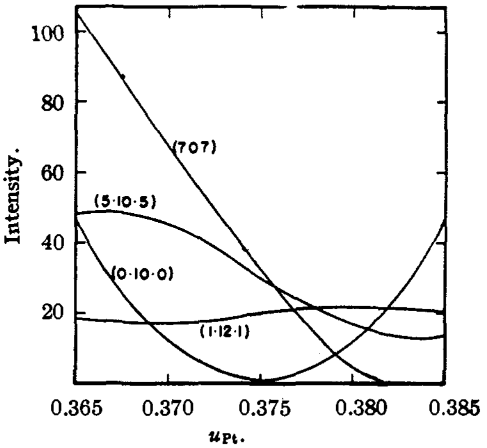

Fig. 5.—Determination of the platinum parameter in tetramethylplatinum.

Discussion of the Structures.—Both compounds are tetramers with the configuration shown in Fig. 2. The platinum atoms and the chlorine atoms or methyls which replace them lie on three-fold axes and have the point symmetry C_{3v}–$3m$. Bonded to each platinum are three carbons; the normal to the plane of the carbons is the three-fold axis on which the platinum lies. The point symmetry of the carbon atoms is C_s–m. There are two of the tetramers per unit cell in a body-centered arrangement, which, for these molecules, is a very close-packed structure (Fig. 3).

Though interatomic distances involving carbon atoms had to be assumed, the following distances are of interest. The platinum–chlorine distance in trimethylplatinum chloride is 2.48 Å., whereas the sum of the covalent radii is 2.30 Å.; the carbon replacing the chlorine is doubtless at a smaller

TABLE II

TETRAMETHYLPLATINUM: INTENSITIES OF EQUATORIAL REFLECTIONS ON [101] ROTATION PHOTOGRAPHS

$h_1h_2h_3$	I'		
	Exp.	Calcd.[a]	Calcd.[b]
$\bar{1}0\bar{1}$	120	135	130
020	0	1	0
$\bar{1}2\bar{1}$	220	210	220
$\bar{2}0\bar{2}$	0	0	0
$\bar{2}2\bar{2}$	590	585	600
040	315	380	385
$\bar{3}0\bar{3}$	260	42	68
$\bar{1}4\bar{1}$		150	105
$\bar{3}2\bar{3}$	190	150	105
$\bar{2}4\bar{2}$	12	7	1
$\bar{4}0\bar{4}$	255	305	310
$\bar{3}4\bar{3}$[c]	150	65	105
$\bar{4}2\bar{4}$	10	3	0
060		6	0
$\bar{1}6\bar{1}$	150	89	110
$\bar{2}6\bar{2}$[c]	380	350	360
$\bar{4}4\bar{4}$	570	475	490
$\bar{5}0\bar{5}$	130	110	68
$\bar{5}2\bar{5}$	290	64	100
$\bar{3}6\bar{3}$		130	93
080	140	165	215
$\bar{1}8\bar{1}$	480	95	85
$\bar{5}4\bar{5}$		185	115
$\bar{4}6\bar{4}$	0	6	0
$\bar{6}0\bar{6}$	18	1	0
$\bar{2}8\bar{2}$		24	0
$\bar{6}2\bar{6}$	460	310	324
$\bar{3}8\bar{3}$[c]	24	40	67
$\bar{5}6\bar{5}$	43	44	88
$\bar{6}4\bar{6}$	14	9	0
$\bar{4}8\bar{4}$	350	285	330
$\bar{7}0\bar{7}$	30	9	44
0.10.0	45	16	0
$\bar{1}.10.\bar{1}$	130	78	94
$\bar{7}2\bar{7}$		120	53
$\bar{2}.10.\bar{2}$	560	238	259
$\bar{6}6\bar{6}$		260	290
$\bar{5}8\bar{5}$	155	29	70
$\bar{7}4\bar{7}$		125	80
$\bar{3}.10.\bar{3}$[c]	185	94	65
$\bar{8}0\bar{8}$	120	114	130
$\bar{8}2\bar{8}$	35	2	0
$\bar{4}.10.\bar{4}$		23	0
$\bar{7}6\bar{7}$	120	87	40
$\bar{6}8\bar{6}$	9	15	0
$\bar{8}4\bar{8}$	345	210	235
0.12.0		125	140
$\bar{1}.12.\bar{1}$	53	55	52
$\bar{5}.10.\bar{5}$	14	40	66
$\bar{2}.12.\bar{2}$	9	26	0
$\bar{3}.12.\bar{3}$	78	30	45
$\bar{7}8\bar{7}$		22	49
$\bar{9}0\bar{9}$		78	38

[a] Calculated for $u_{Pt} = 0.380$. [b] Calculated for $u_{Pt} = 0.375$. [c] The intensity of this reflection is affected especially strongly by the dodecahedral habit of the crystal used; therefore the absorption correction applied in the derivation of $I'_{exp.}$ is unreliable.

distance from platinum than this, but certainly the distance is greater than 2.09 Å., the sum of the platinum and carbon radii. The shortest platinum–platinum distance is 3.73 Å. in trimethylplatinum chloride, 3.44 Å. in tetramethylplatinum. The chlorine–chlorine distance is 3.28 Å. The angle platinum–chlorine–platinum is 99°. Methyl–methyl distances between adjacent tetramers are slightly more than 4 Å. for the parameters chosen.

The unit cell and density data alone are sufficient to indicate that the expected tetrahedral bonding to platinum does not exist in these compounds. The crystals are far too dense to allow the packing of the expected molecules. The fact that tetramethylplatinum is a crystalline compound rather than a low-boiling liquid is added evidence that it is not the ordinary Me_4M compound.

Though the coördinates of the carbon atoms cannot be obtained from the X-ray data there can be no question as to the positions of the platinum atoms. In both compounds, there are sets of four platinum atoms forming regular tetrahedra, each set compact and well separated from neighboring sets. The platinum–platinum distances are too great to permit strong platinum–platinum bonding, but too small for the platinum atoms within the group of four to belong to different molecules. This practically demands that the molecules be tetramers with the platinum bonded through other atoms. In trimethylplatinum chloride it is quite easily established from the X-ray evidence alone that the chlorine atoms are in positions to do this. Though it seems objectionable to bond a methyl group to three platinum atoms there is no other alternative in tetramethylplatinum. This need not mean that carbon violates the octet rule, but it may indicate that the two electrons involved in bonding three platinum atoms to a carbon atom resonate among three possible bonds. In trimethylplatinum chloride the platinum–chlorine distance, 2.48 Å., appears too small for ionic bonding, and it is very doubtful if the unusual methyl bonding can be attributed to a methyl ion.

If the structure described above is accepted, it seems necessary to bond the other methyls to platinum, and thereby to complete the usual octahedral bonding to tetravalent platinum. The packing of the compound is very satisfactory on this basis. The extremely high temperature factors (Tables I and II) are in accord with the hydrocarbon-like packing of the tetramers.

The bridging of platinum to platinum through chlorine in trimethylplatinum chloride is not unlike the reported bridging of aluminum to aluminum through halogens in the aluminum halide dimers.[11,12] It has been suggested that methyls bridge the aluminums in the aluminum methyl dimer. This structure is not in agreement with

---

(11) K. J. Palmer and Norman Elliott, THIS JOURNAL, 60, 1852 (1938).

(12) L. O. Brockway and N. R. Davidson, *ibid.*, 63, 3287 (1941).

published electron diffraction investigations,[12,13] but later, as yet uncompleted, studies in these Laboratories definitely show that the published conclusions are unsatisfactory.[14] Tetramethylplatinum then provides the first established example of a methyl group bonded to more than one other atom.

Acknowledgment.—The authors are indebted to Professor Henry Gilman for supplying crystals of tetramethylplatinum, and for helpful advice and discussions regarding the chemistry of the platinum alkyls and their derivatives. They benefited also from frequent consultations with Professor Linus Pauling.

Summary

The crystal structures of trimethylplatinum chloride and tetramethylplatinum have been determined. The crystals are isomorphic, with space group T_d^3–$I\bar{4}3m$. The edge of the smallest cubic unit is 10.55 Å. for trimethylplatinum chloride and 10.145 Å. for tetramethylplatinum.

Trimethylplatinum chloride is a tetramer with platinum atoms and chlorine atoms at alternate corners of a distorted cube. Bonded to each platinum are three methyl groups. Tetramethylplatinum is similar, with methyls replacing the chlorines. Two of these tetramers, of point symmetry T_d, compose the body-centered unit.

Interatomic distances involving carbon atoms had to be assumed. The distance Pt–Cl = 2.48 Å., Cl–Cl = 3.28 Å., ∠ Pt–Cl–Pt = 99°. The shortest distance Pt–Pt in $PtMe_3Cl$ is 3.73 Å.; in $PtMe_4$ it is 3.44 Å. The Me–Me distances between adjacent tetramers are slightly more than 4 Å.

Tetramethylplatinum provides the first case where a methyl group is bonded to more than one other atom. Neither compound shows the expected d^2sp bonds to platinum.

PASADENA, CALIFORNIA RECEIVED JANUARY 29, 1947

[13] N. R. Davidson, J. A. C. Hugill, H. A. Skinner, and L. E. Sutton, *Trans. Faraday Soc.*, **36**, 1212 (1940).

[14] Private communication from Professor Verner F. H. Schomaker.

[COMMUNICATION NO. 1137 FROM THE KODAK RESEARCH LABORATORIES]

Oxidation Processes. XVIII.[1] A Classification of Reactions on the Basis of the Semiquinone Theory

BY J. E. LUVALLE AND A. WEISSBERGER

The preceding papers of this series dealt with the oxidation of α-ketols (—CHOHCO—), α-aminoketones (—$CHNH_2CO$), enediols (—COH=COH—), and hydroquinones by oxygen and, in some cases, by cupric salts. Kinetic experiments yielded rate laws which were interpreted in terms of reactive species and reaction mechanisms. For instance, it was shown that in these reactions, the mono- and the divalent anions of the various compounds are more reactive than the neutral molecules and that the monomeric products of univalent oxidation, the semiquinones, occupy key positions in the reactions.[1,2] The present paper derives the observed rate laws in a systematic way, making full use of the equilibria in two-step oxidations and of the concept of the steady state. This treatment gives a classification of the earlier results[1,2,3] and furnishes a ready means for the interpretation of more recent data on aromatic amines.[4]

The existence of semiquinones, *i. e.*, of rather stable free radicals which are intermediate in their state of oxidation between *p*- or *o*-diaminobenzenes and quinonediimines, between hydroquinones and quinones, etc., was first suggested by Hantzsch.[5] They were thoroughly studied and discussed by Weitz.[6] Elema[7] and Michaelis[8] showed independently that bivalent oxidations and reductions proceed in univalent steps and that the intermediate semiquinones are in equilibrium with the reduced and the oxidized forms (dismutation) and with their dimers. Both equilibria are in accord with the radical character of the semiquinones. The values of the respective equilibrium constants are functions of the *p*H,[8,9] because dimerization and dismutation of the ions are inhibited by electrostatic repulsion.[8,10] However, the stability of the semiquinones appears to be primarily caused by resonance.[11] The resonance is smaller if the structures are non-equivalent.

[1] Part XVII, Weissberger and LuValle, THIS JOURNAL, **66**, 700 (1944).

[2] (a) James and Weissberger, *ibid.*, **60**, 98 (1938); (b) Weissberger, LuValle and Thomas, *ibid.*, **65**, 1934 (1943).

[3] (a) James, Snell and Weissberger, *ibid.*, **60**, 2084 (1938); (b) Kornfeld and Weissberger, *ibid.*, **61**, 360 (1939).

[4] LuValle and Weissberger, to be published.

[5] Hantzsch, *Ber.*, **49**, 519 (1916); **54**, 1276 (1921).

[6] Weitz, *Z. Elektrochem.*, **34**, 538 (1928).

[7] Elema, *Rec. trav. chim.*, **50**, 807 (1931); **52**, 569 (1933).

[8] (a) Friedheim and Michaelis, *J. Biol. Chem.*, **91**, 355 (1931); (b) Michaelis, *ibid.*, **92**, 211 (1931); (c) Michaelis, THIS JOURNAL, **53**, 2953 (1931); (d) Michaelis, *Chem. Rev.*, **16**, 243 (1935); (e) Michaelis and Schubert, *ibid.*, **22**, 437 (1938); (f) Michaelis and Smythe, *Ann. Rev. Biochem.*, **7**, 1 (1938); (g) Michaelis, *Ann. N. Y. Acad. Sci.*, **40**, 39 (1940).

[9] Michaelis, Granick and Schubert, THIS JOURNAL, **63**, 351 (1941); Michaelis and Granick, *ibid.*, **63**, 1636 (1941); Schubert, *Ann. N. Y. Acad. Sci.*, **40**, 111 (1940).

[10] Weiss, *Trans. Faraday Soc.*, **42**, 116 (1946).

[11] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, 1940, Chap. IV; Wheland, "The Theory of Resonance," John Wiley and Sons, New York, 1944.