

## Organoplatinum compounds

### V \*. Trimethylplatinum bromide. The crystal structure of $[(\text{Me}_3\text{PtBr})_4] \cdot 0.5\text{toluene}$

W. Massa \*, G. Baum, B.-S. Seo and J. Lorberth \*

*Fachbereich Chemie, Philipps-Universität, Lahnberge, Hans-Meerwein-Strasse, D-3550 Marburg/Lahn (West Germany)*

(Received March 21st, 1988)

#### Abstract

Trimethylplatinum bromide crystallizes from toluene as  $[(\text{Me}_3\text{Pt-Br})_4] \cdot 0.5\text{toluene}$  the structure of which has been determined by X-ray diffraction and shown to be of the cubane type observed in the  $(\text{Me}_3\text{Pt-X})_n$  family. Crystal data: space group  $C2/m$ ,  $Z = 4$ ,  $a$  2473.6(3),  $b$  1151.9(1),  $c$  1017.1(1) pm,  $\beta$  109.42(1)°; mean interatomic distances: Pt–Br 267.7 pm, Pt–Pt 393.0 pm, Br–Br 363.2 pm; mean bond angles: Br–Pt–Br 85.4°, (Pt–Br–Pt) 94.3°.

#### Introduction

Of the trialkylplatinum halides  $\text{R}_3\text{PtX}$  all the methyl derivatives except the fluoride “ $\text{Me}_3\text{PtF}$ ” are known, and most of them have been structurally characterized:  $(\text{Me}_3\text{PtCl})_4$  [1], the related  $(\text{Et}_3\text{PtCl})_4$  [2],  $(\text{Me}_3\text{PtI})_4 \cdot \text{C}_6\text{H}_6$  [3], and  $(\text{Me}_3\text{PtI})_4 \cdot \text{CCl}_4$  [4] have almost identical molecular shapes, with systematic variations in the unit cell dimensions depending on the relative sizes of the halogen bridging ligands. These tetrameric structures are also found for pseudohalide or related derivatives, e.g.  $(\text{Me}_3\text{PtN}_3)_4$  [5],  $(\text{Me}_3\text{PtOH})_4$  [6],  $(\text{Me}_3\text{PtSMe})_4$  [7,8]. More recently, tetrameric  $(\text{Me}_3\text{PtSCN})_4$  has been found also to have the tetrameric structure but of a distinctly different type [9].

Deviation from tetrameric association is only found in monomeric  $\text{Me}_3\text{Pt}(\text{C}_5\text{H}_5)$  [10] or in the dimeric 1,3-diketone derivative  $(\text{Me}_3\text{Pt-acac})_2$  [11]. The existence of trimers of (trimethylplatinum)theophylline]  $\cdot \text{L}$  ( $\text{L} = \text{H}_2\text{O}$  or  $\text{HNMe}_2$ ), obtained from chloroform solution, has been postulated on the basis of molecular weight

\* For part IV see ref. 13.

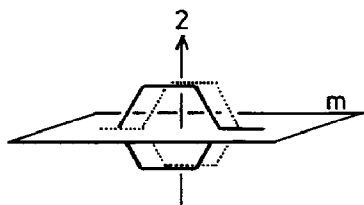
determinations [12], but  $\text{Me}_3\text{Pt}$ -(theophylline) without additional base and recrystallized repeatedly from anhydrous acetonitrile and chloroform gives crystals of the hexameric  $[(\text{Me}_3\text{Pt-tp})_6] \cdot 12\text{CHCl}_3$ , containing both Pt–N and Pt–O bonds [13]. We describe here the crystal and molecular structure of  $[(\text{Me}_3\text{PtBr})_4] \cdot 0.5\text{toluene}$ , to complete the structural characterization of all the trimethylplatinum halides.

### Crystal structure determination

Trimethylplatinum bromide was made as previously described [18] and small pale yellow crystals of  $(\text{Me}_3\text{PtBr})_4 \cdot 0.5\text{C}_7\text{H}_8$  (toluene) were grown from toluene solution. A crystal of dimensions ca.  $0.2 \times 0.1 \times 0.1 \text{ mm}^3$  was used, and examined at 213 K on a four-circle diffractometer (CAD4, Enraf–Nonius, Mo- $K_\alpha$ , graphite monochromator). From 25 high angle reflections the monoclinic lattice constants were refined to  $a$  2473.6(3),  $b$  1151.9(1),  $c$  1017.1(1) pm,  $\beta$  109.42(1)°. From the systematic extinctions  $hkl$ :  $h + k$  odd, the space groups  $C2$ ,  $Cm$ , and  $C2/m$  were all possible, but the centrosymmetric group  $C2/m$  ( $Z = 4$  tetramers,  $d_c$  3.125 g cm<sup>-3</sup>) was shown to be the correct one by successful refinement.

Data collection was performed by  $\omega$ -scans over  $(0.85 + 0.35 \text{ tg}\theta)^\circ$ , with additional 25% on the left-hand and the right-hand side of a reflection for background determination. The measurement time was varied up to 40 s. 2806 reflections in the range of  $1^\circ < \theta < 25^\circ$  ( $h$ : from -29 to +29,  $k$ : from 0 to 13,  $l$ : from -1 to +11) were measured, yielding 1337 independent reflections with  $F_o > 5\sigma(F_o)$ . All calculations were performed on a MikroVAXII computer. The structure was solved by Direct Methods [14] and subsequent difference Fourier syntheses; full matrix least square methods [15] were used for further refinement. Owing to some decomposition of the crystal after data collection was finished, the necessary absorption correction ( $\mu$  264 cm<sup>-1</sup>) was made by the method described by Walker and Stuart (DIFABS [16]). Anisotropic temperature factors were refined for the platinum and bromine atoms.

Along with every  $(\text{Me}_3\text{PtBr})_4$  tetramer we found half a molecule of toluene, disordered on sites of symmetry  $2/m$  ( $C_{2h}$ ); two alternative orientations are related by the twofold axis (see Scheme 1). Independent refinement was impossible due to



Scheme 1. Orientation of two molecules of toluene: disordered model on sites of symmetry  $2/m$  ( $C_{2h}$ ).

the partial mutual overlap of atomic positions, and so the atomic coordinates for the disordered model were calculated starting from atom positions indicated by the maxima in a difference Fourier map assuming idealized toluene geometry. In the refinement process only isotropic temperature factors were included. The final  $R$ -factors were  $R = 0.0475$ ,  $R_w = 0.0351$  (weights  $w = 1/\sigma^2(F_o)$ ); minimized functions  $\sum w(|F_o| - |F_c|)^2$ .

## Discussion

The resulting positional and equivalent isotropic temperature factors are given in Table 1, and selected interatomic distances and bond angles in Table 2\*.

Figure 1 shows the (distorted) cubane-like structure of the tetrameric  $(\text{Me}_3\text{PtBr})_4$  unit, which is similar to those of some other trimethylplatinum halides and pseudo-halides (Tab. 3). Hydrogen atoms are omitted.

Figure 2 presents a perspective view of two adjacent unit cells including the toluene molecules: double layers of tetrameric units, separated by disordered toluene molecules, are stacked along the [100] direction. The symmetry of the tetramer is  $m$  ( $S_{1h}$ ), with pseudosymmetry  $43m$  ( $T_d$ ); Pt(1), Pt(2), Br(2) and Br(3) are on the mirror plane. The deviations from the higher symmetry are very small, the lower crystallographic symmetry is attributable to the special packing pattern (cf. Fig. 2).

Comparison of the geometry of the trimethylplatinum bromide tetramer with those for the corresponding chloride and iodide reveals that it falls in an intermediate position, as expected. The angular distortions of the cube are small, and close to those of the iodide. The shortest intermolecular contacts between two

Table 1

Positional and equivalent isotropic thermal parameters for  $[(\text{Me}_3\text{PtBr})_4] \cdot 0.1\text{C}_7\text{H}_8$ .

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Atom	x	y	z	$U_{\text{eq}}$
Pt(1)	0.62619(5)	0.5	0.43202(17)	0.0245(6)
Pt(2)	0.76939(6)	0.5	0.34497(18)	0.0235(5)
Pt(3)	0.63473(4)	0.67105(10)	0.10669(13)	0.0296(4)
Br(1)	0.69463(10)	0.6569(2)	0.37690(30)	0.0270(9)
Br(2)	0.57055(15)	0.5	0.1571(4)	0.0312(16)
Br(3)	0.70350(15)	0.5	0.0743(5)	0.0357(16)
C(11)	0.5726(10)	0.617(2)	0.471(3)	0.039(7)
C(12)	0.6734(15)	0.5	0.642(4)	0.039(11)
C(21)	0.8248(10)	0.615(2)	0.319(3)	0.044(8)
C(22)	0.8155(15)	0.5	0.535(4)	0.047(12)
C(31)	0.5807(11)	0.795(2)	0.133(3)	0.043(8)
C(32)	0.5891(9)	0.678(2)	-0.099(3)	0.036(7)
C(33)	0.6871(11)	0.801(2)	0.073(3)	0.058(9)
Disordered toluene (site occupation factors 0.5)				$U$
C(1)	0.0016	0.3994	0.5219	0.067(16)
C(2)	0.0169	0.5	0.7342	0.06(3)
C(3)	0.0065	0.5	0.5875	0.25(9)
C(4)	-0.0081	0.3994	0.3907	0.036(14)
C(5)	-0.0129	0.5	0.3337	0.05(3)

\* A complete table of structural parameters and lists of anisotropic temperature parameters and structure factors may be obtained from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen, F.R.G., under specification of deposit no. CSD 53174, authors, and journal reference.

Table 2

Selected interatomic distances (pm) and angles ( $^{\circ}$ ) for  $[(\text{Me}_3\text{PtBr})_4] \cdot 0.5\text{C}_7\text{H}_8$ 

Pt(1)–Br(1) 2 ×	266.0(3)	Pt(1)–C(11) 2 ×	202(2)
Pt(1)–Br(2)	267.5(4)	Pt(1)–C(12)	207(4)
Pt(2)–Br(1) 2 ×	268.2(3)	Pt(2)–C(21) 2 ×	199(2)
Pt(2)–Br(3)	269.3(5)	Pt(2)–C(22)	189(4)
Pt(3)–Br(1)	265.8(3)	Pt(3)–C(31)	203(3)
Pt(3)–Br(2)	268.5(3)	Pt(3)–C(32)	202(3)
Pt(3)–Br(3)	269.4(3)	Pt(3)–C(33)	208(2)
mean Pt–Br	267.7	mean Pt–C	201
Pt(1)...Pt(2)	393.5(1)	Br(1)...Br(1')	361.5(5)
Pt(1)...Pt(3) 2 ×	391.7(2)	Br(1)...Br(2) 2 ×	362.2(5)
Pt(2)...Pt(3) 2 ×	393.5(2)	Br(1)...Br(3) 2 ×	363.8(6)
Pt(3)...Pt(3')	394.1(2)	Br(2)...Br(3)	365.6(6)
mean Pt...Pt	393.0	mean Br...Br	363.2
Br(1)–Pt(1)–Br(1')	85.6(1)	Pt(1)–Br(1)–Pt(2)	94.6(1)
Br(1)–Pt(1)–Br(2)	85.5(1)	Pt(1)–Br(1)–Pt(3)	94.9(1)
Br(1)–Pt(2)–Br(1')	85.2(1)	Pt(2)–Br(1)–Pt(3)	94.9(1)
Br(1)–Pt(2)–Br(3)	84.8(1)	Pt(1)–Br(2)–Pt(3)	93.9(1)
Br(1)–Pt(3)–Br(3)	85.6(1)	Pt(3)–Br(2)–Pt(3')	94.4(1)
Br(2)–Pt(3)–Br(3)	85.7(1)	Pt(2)–Br(3)–Pt(3)	93.9(1)
mean Br–Pt–Br	85.4	Pt(3)–Br(3)–Pt(3')	94.0(1)
		mean Pt–Br–Pt	94.3

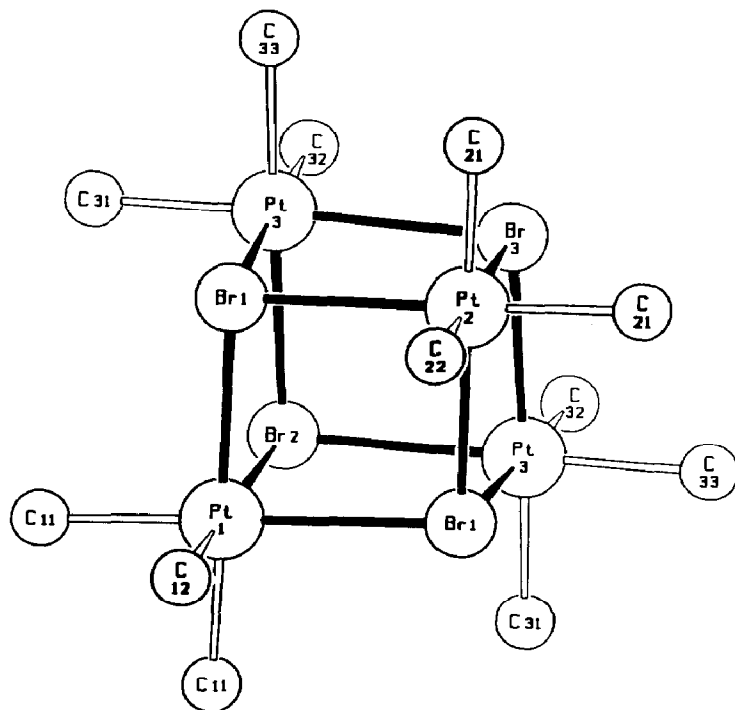
Fig. 1. SCHAKAL [17] plot of the structure of tetramer  $[(\text{Me}_3\text{PtBr})_4]$  in the crystal, showing the atom numbering.

Table 3

Comparison of typical molecules parameters in the complexes  $[(Me_3PtX)_4]$  (X = halide, pseudohalide, or related ligands)

X	Pt-X (pm)	Pt-Pt (pm)	X-X (pm)	X-Pt-X (°)	Pt-X-Pt (°)	Pt-C (pm)	Ref.
Cl	248	373	328	81.0	99.0	209	[1]
Br	268	393	363	85.4	94.3	201	this work
I	281.9	411	385.2	86.2	93.7	202	[4]
OH	222	342.0	278	77.6	101.2	204	[6]
N <sub>3</sub>	225	344.9		80.0	100.0	205	[5]
SCN	255(S) 208(N)	383		82.4	97.3	203	[9]
SCH <sub>3</sub>	247 217(N)	378.0	315	79.3	99.1	207	[8]
thp <sup>a</sup>	221(N) 234(O)			82.0		206	[13]

<sup>a</sup> thp = denotes the anion from theophylline, hexameric structure.

adjacent tetramers are those between bromine atoms Br(1)...Br(1') (372 pm) and Br(2)...Br(2') (387 pm), distances close to the sum of the Van der Waals radii (370 pm).

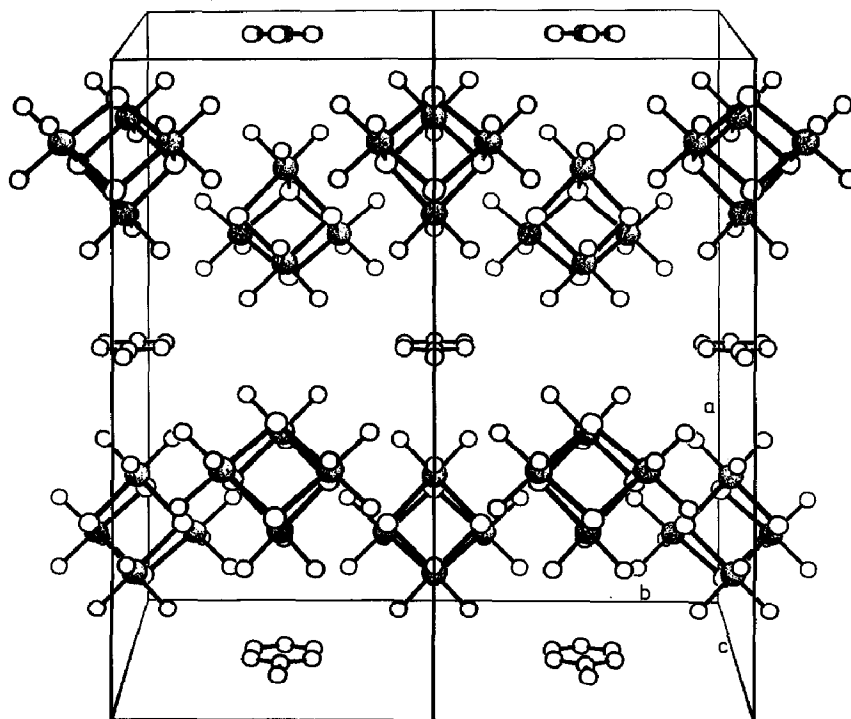


Fig. 2. Perspective view of two unit cells (SCHAKAL [17]). For clarity only one orientation of the toluene molecules is shown.

## Acknowledgement

We thank the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie e.V. for support of this work, and DEGUSSA, Hanau for a generous gift of the platinum complex used as the starting material.

## References

- 1 R.E. Rundle and J.D. Sturdivant, *J. Am. Chem. Soc.*, 69 (1947) 1561.
- 2 R.N. Hargreaves and M.R. Truter, *J. Chem. Soc. A*, (1971) 90.
- 3 G. Donnay, L.B. Coleman, N.G. Kriehoff and D.O. Cowan, *Acta Cryst.*, B, 24 (1968) 287.
- 4 R. Allmann and D. Kucharczyk, *Z. Krist.*, 165 (1983) 227.
- 5 M. Atam and U. Müller, *J. Organomet. Chem.*, 71 (1974) 435.
- 6 H.S. Preston, J.C. Mills and C.H.L. Kennard, *J. Organomet. Chem.*, 14 (1968) 447.
- 7 G. Smith, C.H. Kennard and T.C. Mak, *J. Organomet. Chem.*, 290 (1985) C7.
- 8 H. Herdtweck, B.S. Seo, H. Donath and J. Lorberth, *J. Organomet. Chem.*, in press.
- 9 B. Vance, *J. Organomet. Chem.*, 336 (1987) 441.
- 10 G.W. Adamson, J.C.J. Bart and J.J. Daly, *J. Chem. Soc. A*, (1971) 2616.
- 11 A.G. Swallow and M.R. Truter, *Proc. Roy. Soc. A*, 252 (1960) 205; A.C. Hazell and M.R. Truter, *Proc. Roy. Soc. A*, 252 (1960) 218.
- 12 N.H. Agnew, T.G. Appleton, J.R. Hall, G.F. Kilmister and I.J. McMahon, *J. Chem. Soc. Chem. Commun.*, (1979) 324.
- 13 L. Labib, M. El-Essawi, W. Massa and J. Lorberth, *Angew. Chem.*, in press.
- 14 G.M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, Göttingen, 1986.
- 15 G.M. Sheldrick, SHELX76, Program for Crystal Structure Determination, Cambridge, 1976.
- 16 N. Walker and D. Stuart, *Acta Crystallogr. A*, 39 (1983) 158.
- 17 E. Keller, Schakal86b, A FORTRAN Program for the Graphical Representation of Molecular and Crystallographic Models, Freiburg 1986.
- 18 J. Pope and J.S. Peachey, *J. Chem. Soc. (London)*, 95 (1909) 571.