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Organoplatinum compounds: VI[1]. Trimethylplatinum thiomethylate and trimethylplatinum iodide. The crystal structures of $[(CH_3)_3PtS(CH_3)]_4$ and $[(CH_3)_3PtI]_4 \cdot 0.5CH_3I$[2]

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Abstract

During the course of our platinum cluster investigations $[(CH_3)_3PtS(CH_3)]_4$ (**1**) was synthesized according to Hall et al. (J.R. Hall, D.A. Hirons, G.A. Swile, J. Organomet. Chem. 174 (1979) 355) [1] from $[(CH_3)_3Pt(H_2O)_3]^{2+}$ SO_4^{2-} and SCH_3^- ions in aqueous solution; $[(CH_3)_3PtI]_4 \cdot 0.5CH_3I$ (**2**) was obtained as the first logically derived product from the oxidative addition of CH_3I to $CODPt(CH_3)_2$ in pure CH_3I solution as transparent yellow crystals (COD = 1,5-cyclooctadiene). Compound (**1**) crystallizes in space group $P\bar{3}c1$ and (**2**) in space group $R\bar{3}$. Compound (**1**) is isostructural with tetrakis(trimethylplatinum azide) {(a) M. Atam, U. Müller, J. Organomet. Chem. 71 (1974) 435 and (b) K.-H. von Dahlen, J. Lorberth, J. Organomet. Chem. 65 (1974) 267} [2]; both the iodine and azide compounds have four tetramers in the unit cell. The unit cell dimensions of (**1**) are: $a = b = 1044(2)$ and $c = 3208(2)$ pm. For (**2**) we observe 12 tetramers in the unit cell and disordered solvent CH_3I in a 2:1 ratio resulting in a huge cell volume extremely extended along the c-axis with > 90 Å: $a = b = 1021.39(4)$ and $c = 9055.5(8)$ pm. X-ray diffraction data refinements converged at $R = 0.048$ and $Rw = 0.039$ for $[(CH_3)_3PtS(CH_3)]_4$ and at $R = 0.0599$ and $wR_2 = 0.1013$ for $[(CH_3)_3PtI]_4 \cdot 0.5CH_3I$. A distorted 'cubane skeleton' is found for $[(CH_3)_3PtS(CH_3)]_4$ with octahedrally coordinated platinum atoms and tetrahedrally coordinated sulfur atoms. In (**2**) we have a similar skeleton but with two independent tetrameric molecules in the unit cell.

Keywords: Platinum; Organoplatinum compounds; Platinum thiolate; Platinum iodide; Crystal structure; Platinum metal group

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1. Introduction

Following our earlier structural studies in the 'cubane' cluster chemistry of platinum(IV) compounds we reported in 1983 on the synthesis and crystal structure of $[(CH_3)_3PtI]_4 \cdot CCl_4$ [3] and provided some preliminary information [4] on the 'cubane' geometry of the newly synthesized tetramer $[(CH_3)_3PtS(CH_3)]_4$ (**1**); our results were later confirmed by Kennard et al. in a short communication [5]. Here we describe the details of preparation and the crystal structure solution in a wider context together with our earlier results, but particularly together with the X-ray investigation of crystals of the first isolable solvate from the oxidative addition reaction of $CODPtMe_2$ with CH_3I as a solvent, affording $[Me_3PtI]_4 \cdot 0.5CH_3I$. The whole series of trimethylplatinum halide derivatives $[Me_3PtX]_4$ for X = fluorine [6], chlorine [4], bromine [7] and iodine [3] has been completed; apart from the azide [2] and the thiocyanide [8] derivates, no other pseudohalides have come to our attention. However, credit should be given to the

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[1] For part V see [8].

[2] Dedicated to Prof. Dr B. Kadenbach on the occasion of his 65th birthday in recognition of his pioneering contributions to the field of 'Ageing Research'.

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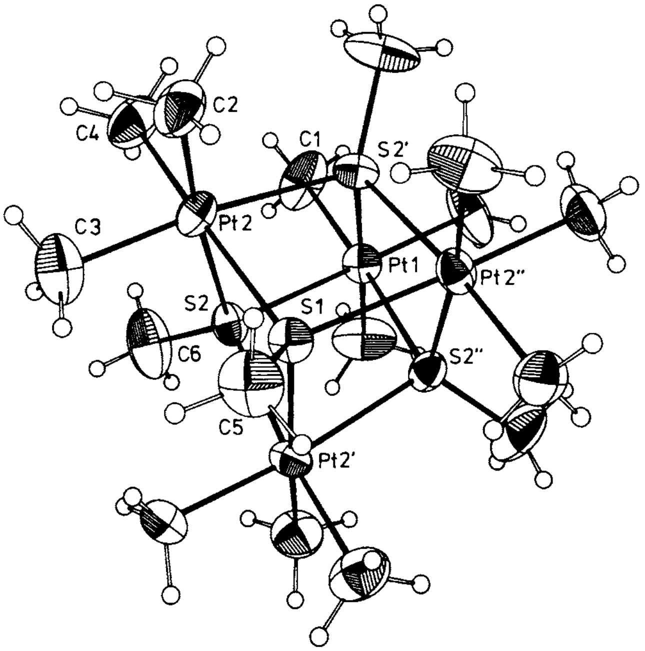

Fig. 1. ORTEP [11] view of the 'cubane type' molecular structure of $[(CH_3)_3PtS(CH_3)]_4$ (**1**). The 3-fold axis passes through C5, S1 and Pt1. Primed atoms refer to $(1-y,\ 1+(x-y),\ z)$ symmetry while doubly primed atoms refer to $(y-x,\ 1-x,\ z)$. Displacement ellipsoids are at the 50% probability level.

first acceptable structure suggestion by Donnay et al. [9] which dominated the textbook literature since then for the terminus technicus 'platinum cluster' in organometallic chemistry.

2. Results and discussion

The reported methylthiolate compound $[(CH_3)_3PtS(CH_3)]_4$ (**1**) shows no remarkable deviations in the overall geometry and the molecular packing of the 'cubane' clusters (Fig. 1) to the isostructural azide derivative $[Me_3PtN_3]_4$ [2]. According to the fact, that the $S(CH_3)$– ligand is a bulkier group than the linear azide skeleton, Pt···Pt distances increase from 345 to 378 pm (average distance). Otherwise, the overall geometry of the Pt–S skeleton is still characterized by an arrangement of octahedrally coordinated platinum atoms and a tetrahedral environment at the sulfur atoms, resulting in a significant distortion of the Pt_4S_4 cubes, therefore coined 'cubanes'; Kennard et al. [5] reported a similar structure which fits perfectly our own results. Geometrical aspects, e.g. atomic distances and bond angles of a whole series of $[Me_3PtX]_4$ compounds now available are summarized in Table 4.

In $[(CH_3)_3PtI]_4\cdot 0.5CH_3I$ (**2**) we observed the same 'cubane' cluster (see Fig. 2) as described for the chloride [4] and for the iodide reported by Allmann et al. [3]; a literature extract is also compiled in Table 4. In the asymmetric unit of **2** we find two independent tetrameric clusters with C_3 symmetry and one molecule of disordered CH_3I in a 2:1 ratio. Near to Pt(1) and Pt(4) we observe a high residual electron density: the near distance to platinum allows for the interpretation as an iodine atom which has oxidized ca. 2% of the Pt(1) and Pt(4) atoms. Likewise we found also a high residual electron density near Pt(2) and Pt(3) in the asymmetric unit which could be explained by disorder of the methyl groups.

Pt-I distances in both molecules approach an average value of 282.4(1) pm; this distance is only 0.5 pm longer than in the iodide tetramer with CCl_4 as a solvate molecule [3]. The unit cell of **2** is extraordinarily elongated along the *c*-axis with 9055.5(8) pm (**!**) and includes 12 tetramers and six disordered CH_3I molecules (Figs. 2 and 3). The cubane-like moieties are arranged to layers which are stacked in a 12 L mode ABCACABCBCAB (Fig. 2). Every second layer the disordered CH_3I molecules are inserted.

These findings support our earlier statement that $[Me_3PtX]_4$ derivatives form suitable crystals often with a minimum amount of solvent molecules which are interlayered, as demonstrated in the case of $[Me_3PtBr]_4\cdot 0.5C_6H_5CH_3$ [7] or $[Me_3PtI]_4\cdot CCl_4$ [3]; if these solvent molecules are removed in vacuo the crystals crumble to an amorphous powder.

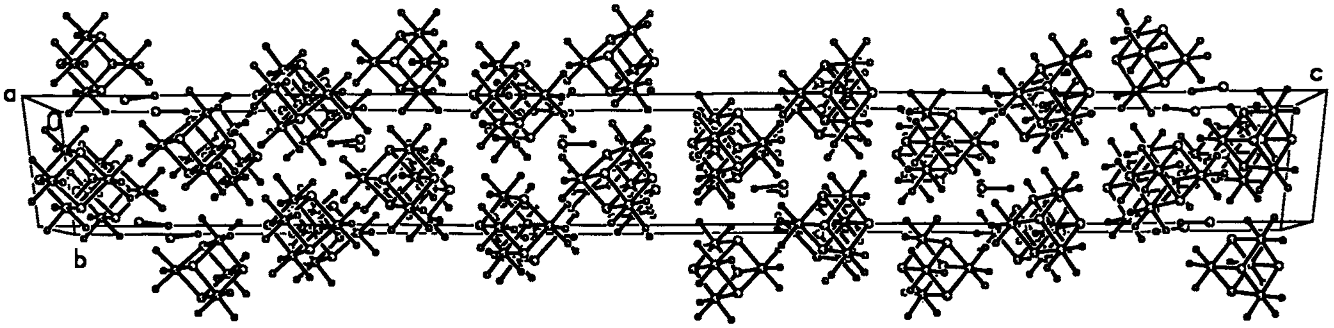

Fig. 2. Stereo plot of the cell of $[(CH_3)_3PtI]_4\cdot 0.5CH_3I$.

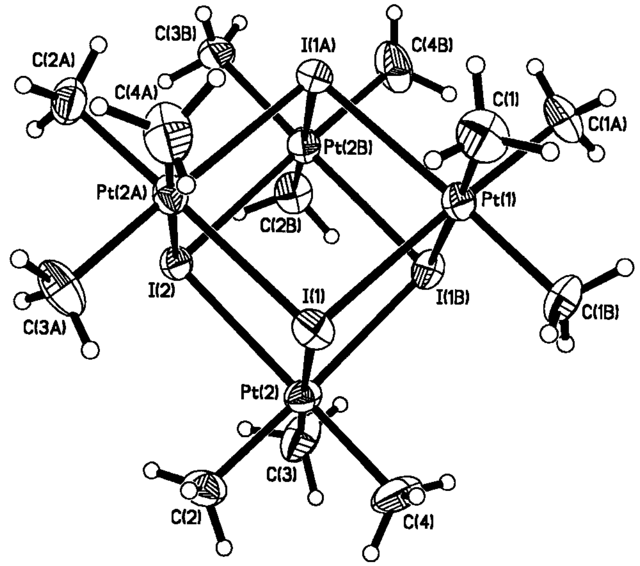

Fig. 3. ORTEP [11] view of the 'cubane type' molecular structure of $[(CH_3)_3PtI]_4$ (**2**). Displacement ellipsoids are at the 50% probability level.

3. Experimental section

3.1. Crystal structure determination

3.1.1. $[Me_3PtSMe]_4$ (1)[3]

Crystal data together with the details of the X-ray diffraction experiment are reported in Table 1. Preliminary films of (**1**), taken on a Burger precession camera, showed a trigonal symmetry with systematic absences: $h-hl$: $l=2n+1$ in agreement with space group $P3c1$ (int. table no. 158) or $P\bar{3}c1$ (int. table no. 165). The latter one was confirmed during refinement. Orientation matrix and cell dimensions were obtained from least squares refinement using a set of 24 reflections in the range $8.2 \leq 2\theta \leq 38.8°$. During data collection no deorientation or decay was detected. Intensities were corrected for Lorentz and polarization effects, and a numerical absorption correction based upon eight faces was applied. The platinum atom positions were determined from the Patterson map and all non-H atoms were located by successive structure factor calculations and difference Fourier maps. Hydrogen atoms were not found, their fixed positions (C–H 100 pm) were added to the calculations, but not refined. Refinements converged with non-weighted and weighted residuals $R=0.048$ and $R_w=0.038$, respectively. For a satisfactory, complete analysis, the criterion was the absence of significant features in the final difference map [10,11]. Selected bond lengths and bond angles are given in Table 2.

Table 1
Crystallographic data for **1** and **2**

	1	**2**
Empirical formula	$C_{16}H_{48}Pt_4S_4$	$C_{12.5}H_{37.5}I_{4.5}Pt_4$
Formula weight (g mol^{-1})	1149.2	1539.33
Crystal color and shape	Colorless prism	Colorless block
Crystal size (mm)	0.12 × 0.25 × 0.30	0.12 × 0.10 × 0.06
Crystal system	Trigonal	Rhombohedral
Space group	$P\bar{3}c1$ (no. 165)[a]	$R\bar{3}$ (no. 148)[a]
Unit cell dimensions		
a (Å)	10.44(2)	10.2139(4)
b (Å)	10.44(2)	10.2139(4)
c (Å)	32.08(6)	90.555(8)
V (Å^3)	3029	8181.4(9)
Z	4	12
$D_{calc.}$ (mg m^{-3})	2.520	3.749
Absorption coefficient (mm^{-1})	17.95	25.544
$F(000)$		7956
R^b	0.048	0.0599
R_w^c	0.039	
wR_2^d		0.0993
Largest difference peak and hole (e Å^{-3})		4.2 and −2.8

[a] International tables.
[b] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[c] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{0.5}$.
[d] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/wF_o^4]^{0.5}$.

Table 2
Selected bond lengths and angles for $[Me_3PtSMe]_4$ (1)

Bond distances (pm)			
Pt(1)···Pt(2)	378.1(1)	Pt(2)–S(2′)	248.1(5)
Pt(2)···Pt(2′)	377.9(1)	Pt(2)–C(2)	205(2)
Pt(1)–S(1)	247.1(4)	Pt(2)–C(3)	207(2)
Pt(1)–C(1)	208(2)	Pt(2)–C(4)	207(2)
Pt(2)–S(1)	246.5(3)	S(1)–C(5)	180(3)
Pt(2)–S(2)	246.6(5)	S(2)–C(6)	180(3)
Bond angles (°)			
S(2)–Pt(1)–S(2′)	79.4(7)	Pt(2)–S(1)–Pt(2″)	100.1(1)
S(2)–Pt(1)–C(1)	95.7(7)	Pt(2)–S(1)–C(5)	117.7(6)
S(2′)–Pt(1)–C(1′)	96.8(7)	Pt(1)–S(2)–Pt(2)	99.9(1)
S(2″)–Pt(1)–C(1)	174.2(7)	Pt(1)–S(2)–Pt(2′)	99.5(1)
C(1)–Pt(1)–C(1)	87.9(9)	Pt(1)–S(2)–C(6)	117.5(7)
S(1)–Pt(2)–S(2)	79.3(1)	Pt(2)–S(2)–Pt(2′)	99.6(1)
S(1)–Pt(2)–S(2′)	79.0(1)	Pt(2)–S(2)–C(6)	118.5(7)
S(1)–Pt(2)–C(2)	96.1(7)	Pt(2′)–S(2)–C(6)	117.7(9)
S(1)–Pt(2)–C(3)	95.7(7)	S(2′)–Pt(2)–C(2)	95.7(7)
S(1)–Pt(2)–C(4)	174.0(7)	S(2′)–Pt(2)–C(3)	173.0(7)
S(2)–Pt(2)–S(2′)	79.3(1)	S(2′)–Pt(2)–C(4)	96.9(6)
S(2)–Pt(2)–C(2)	173.8(7)	C(2)–Pt(2)–C(3)	89.4(9)
S(2)–Pt(2)–C(3)	95.3(7)	C(2)–Pt(2)–C(4)	88.7(9)
S(2)–Pt(2)–C(4)	95.6(6)	C(3)–Pt(2)–C(4)	88.0(9)

′ $(1-y,\ 1+(x-y),\ z)$ and ″ $(y-x,\ 1-x,\ z)$ symmetry.

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[3] Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D-76344 Eggenstein- Leopoldshafen, Germany, on quoting the deposit numbers CSD-53366 (**1**) and CSD-408053 (**2**), the names of the authors and the journal citation.

Table 3
Selected bond lengths and angles for $[(CH_3)_3PtI]_4 \cdot 0.5CH_3I$ (2)

Molecule 1			
Bond lengths (pm)			
Pt(1)–I(1)	283.12(8)	Pt(2)–I(1″)	281.05(8)
Pt(1)–C(1)	206.2(14)	Pt(2)–C(2)	205.2(13)
Pt(2)–I(1)	283.08(8)	Pt(2)–C(3)	207.8(12)
Pt(2)–I(2)	283.66(7)	Pt(2)–C(4)	204.5(13)
Bond angles (°)			
I(1)–Pt(1)–I(1′)	86.36(3)	I(1)–Pt(2)–C(4)	91.4(5)
I(1)–Pt(1)–I(1″)	86.36(3)	I(2)–Pt(2)–C(2)	90.4(4)
I(1)–Pt(1)–C(1)	95.5(4)	I(2)–Pt(2)–C(3)	94.1(4)
I(1′)–Pt(1)–C(1)	90.7(4)	I(2)–Pt(2)–C(4)	178.0(5)
I(1″)–Pt(1)–C(1)	176.4(4)	C(2)–Pt(2)–C(3)	89.0(6)
C(1)–Pt(1)–C(1′)	87.5(6)	C(2)–Pt(2)–C(4)	89.1(6)
Pt(2′)–I(2)–Pt(2″)	92.67(3)	C(3)–Pt(2)–C(4)	87.8(6)
I(1)–Pt(2)–I(2)	86.73(2)	Pt(1)–I(1)–Pt(2)	93.11(2)
I(1″)–Pt(2)–I(1)	86.77(3)	Pt(1)–I(1)–Pt(2′)	93.54(2)
I(1″)–Pt(2)–I(2)	87.11(2)	Pt(2)–I(1)–Pt(2′)	93.33(3)
I(1)–Pt(2)–C(2)	92.9(4)	Pt(2)–I(2)–Pt(2′)	92.66(3)
I(1)–Pt(2)–C(3)	178.0(4)	Pt(2)–I(2)–Pt(2″)	92.67(3)
Molecule 2			
Bond lengths (pm)			
Pt(3)–I(3)	283.30(7)	Pt(3)–C(6)	206.4(12)
Pt(3)–I(4)	282.73(8)	Pt(3)–C(7)	206.3(13)
Pt(3)–I(4‴)	281.85(8)	Pt(4)–I(4)	283.02(8)
Pt(3)–C(5)	203.9(12)	Pt(4)–C(8)	207.2(13)
Bond angles (°)			
I(3)–Pt(3)–I(4)	86.76(2)	I(4)–Pt(4)–I(4‴)	86.48(3)
I(4‴)–Pt(3)–I(4)	86.75(3)	I(4)–Pt(4)–I(4⁗)	86.48(3)
I(4‴)–Pt(3)–I(3)	86.93(2)	I(4)–Pt(4)–C(8)	176.0(4)
I(4)–Pt(3)–C(5)	94.2(4)	I(4‴)–Pt(4)–C(8)	90.3(4)
I(4)–Pt(3)–C(6)	91.1(4)	I(4⁗)–Pt(4)–C(8)	95.8(4)
I(4)–Pt(3)–C(7)	177.1(4)	C(8)–Pt(4)–C(8‴)	87.5(6)
I(3)–Pt(3)–C(5)	177.1(4)	Pt(3)–I(3)–Pt(3‴)	92.86(3)
I(3)–Pt(3)–C(6)	94.1(4)	Pt(3)–I(3)–Pt(3⁗)	92.86(3)
I(3)–Pt(3)–C(7)	90.4(4)	Pt(3‴)–I(3)–Pt(3⁗)	92.86(3)
C(5)–Pt(3)–C(6)	88.6(6)	Pt(3)–I(4)–Pt(4)	93.19(2)
C(5)–Pt(3)–C(7)	88.6(6)	Pt(3)–I(4)–Pt(3⁗)	93.29(3)
C(6)–Pt(3)–C(7)	89.4(6)	Pt(4)–I(4)–Pt(3⁗)	93.38(2)

′ $(-y+1, x-y, z)$, ″ $(-x+y+1, -x+1, z)$, ‴ $(-x+y, -x, z)$ and ⁗ $(-y, x-y, z)$ symmetry.

3.1.2. $[(CH_3)_3PtI]_4 \cdot 0.5CH_3I$ (2)[iii]

The crystal data of (**2**) are also reported in Table 1, bond lengths and angles are shown in Table 3.

Diffraction data were collected on a Stoe IPDS area detector system at 193 K with Mo–K_α radiation, $\lambda = 0.71073$ Å, for 40014 reflections. A total of 5318 reflections were independent ($R_{int} = 0.1092$) and were used in a full-matrix least-squares refinement on F^2 with the SHELXL-97 program package [12]. The structure was solved with direct methods for the platinum and the iodine atoms and a difference fourier synthesis revealed the position of the light atoms. Hydrogen atoms were calculated using a 'riding model' with isotropic thermal parameters; a numerical absorption correction was applied (max and min transmission 0.40 and 0.36).

3.2. Preparation of compounds

3.2.1. $[Me_3PtSMe]_4$ (1)

A 5.00 g (13.6 mmol) sample of Me_3PtI and 2.12 g (6.8 mmol) Ag_2SO_4 were refluxed in a solvent mixture of 100 ml acetone with 50 ml benzene for 8 h. AgI was separated by filtration and was washed several times with acetone in small portions. This was followed by evaporating to dryness and the residue was dissolved in 200 ml water. Precipitation of Me_3PtSMe occurred by carefully adding an aqueous solution of NaSMe; in this step only a minor excess of the thiolate was applied. Filtration and extraction of the yellow–brown solid with 50 ml of benzene under refluxing for 3 h afforded a microcrystalline powder which was dissolved in a minimum amount of chloroform and again filtered. Addition of small amounts of ethanol yielded a yellow, crystalline product in an overall yield of 75–80%, based on the amount of Me_3PtI used. Anal. Calc.: C 16.75, H 4.21, S 11.17. Found: C 16.92, H 4.01, S 10.84%.

3.2.2. $[(CH_3)_3PtI]_4 \cdot 0.5CH_3I$ (2)

A 5.00 g (150 mmol) sample of $CODPtMe_2$ was dissolved in 30 ml of pure, distilled CH_3I, the flask was

Table 4
Comparison of trimethylplatinum structures exhibiting a 'cubane skeleton' $[Me_3PtX]_4$

X	Pt-X	Pt···Pt	X···X	X-Pt-X	Pt-X-Pt	Pt-C	Ref.
F	225.1(6)	345.4	285.5	78.7(4)	100.2(3)	200.9(10)	[6]
Cl	248(11)	373	328	81	99	205.7	[4]
Br	267.7	393.0	363.2	85.4	94.3	201	[7]
I	282.4(1)	410.5(1)	387.8(2)	86.6(3)	93.1(3)	205.9(13)	This paper
I	281.9(6)	411.2	385.2	86.2	93.7	202	[3]
N_3	225(5)	344.9(4)	289	80	100	205(6)	([2]a)
OH	221.7(5)	343.53(5)	276.5(9)	77.1(4)	101.6(3)	202.6(8)	[6]
OH	222(1)	343.0	278	77.6	101.2	204	[13]
S–Me	247.1(4)	378.0	315.2	79.3(3)	99.1(1)	207(2)	This paper
S–Me	248(2)	380(2)	310.7	79.1(7)	102.3	200(4)	[5]
S–CN[a]	255(2)	383	337.6	82.4(6)	97.3(6)	203	[8]

Average values of distances in pm, angles in degrees and available estimated S.D. in parenthesis.

[a] This is not a cubane structure, but the rectangular skeleton shows Pt–S and Pt–N coordination

wrapped in aluminum foil for light protection and the clear solution left undisturbed for 10 days, after which tiny, transparent crystals began to form, growing by time to bulk, transparent blocks of $Me_3PtI \cdot 0.5CH_3I$, according to elemental analysis and confirmation by X-ray investigation.

Table 4 summarizes the atomic distances and bond angles of a whole series of $[Me_3PtX]_4$ compounds.

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