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Tetra-μ_3-bromido-tetrakis[trimethylplatinum(IV)]

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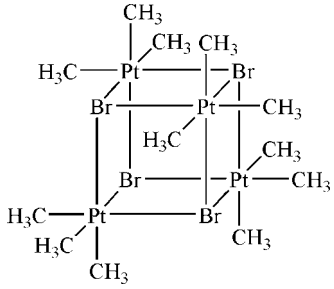
Key indicators: single-crystal X-ray study; T = 243 K; mean σ(t–C) = 0.010 Å; R factor = 0.033; wR factor = 0.078; data-to-parameter ratio = 26.5.

The title complex, $[Pt_4Br_4(CH_3)_{12}]$, the tetramer of trimethylplatinum(IV) bromide, reveals a distorted cubane-like structure and is disposed about a crystallographic mirror plane passing through two Pt atoms, two Br atoms and two methyl groups parallel to the *ac* plane. The tetrameric complex displays pseudo-cubic molecular symmetry, $\overline{4}3m$. The coordination geometry around each Pt centre is distorted octahedral. The tetrameric units in the crystal structure are packed by hydrophobic interactions or van der Waals contacts.

Related literature

For historical background, see: Rundle & Sturdivant (1947); Atam & Müller (1974). For the corresponding tetrameric trimethylplatinum(IV) bromide with disordered toluene solvent, see: Massa *et al.* (1988). For related literature, see: Cowan *et al.* (1968); Donath *et al.* (1998); Preston *et al.* (1968); Spiro *et al.* (1968).



Experimental

Crystal data

$[Pt_4Br_4(CH_3)_{12}]$
M_r = 1280.41
Monoclinic, $C2/m$
a = 13.8146 (12) Å
b = 14.0793 (12) Å
c = 12.8194 (11) Å
β = 95.681 (2)°
V = 2481.1 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 28.92 mm^{-1}
T = 243 (2) K
0.15 × 0.10 × 0.08 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.053, T_{max} = 0.099
7252 measured reflections
2655 independent reflections
2189 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.078
S = 0.98
2655 reflections
100 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.37 e Å^{-3}
$\Delta\rho_{min}$ = −1.86 e Å^{-3}

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2029).

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supplementary materials

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Tetra-μ_3-bromido-tetrakis[trimethylplatinum(IV)]

A.-R. Song, I.-C. Hwang and K. Ha

Comment

Trimethylplatinum(IV) halides, hydroxide and pseudohalides reveal structures of cubane-like clusters with the tetrameric unit, [{Pt(CH_3)$_3$L}$_4$] (*L* = F, Cl, Br, I, OH, N_3 *etc*.), and the tetrameric units show approximately −43*m* symmetry. F (Donath *et al.*, 1998), Cl (Rundle & Sturdivant, 1947) and OH clusters (Cowan *et al.*, 1968; Spiro *et al.*, 1968; Preston *et al.*, 1968; Donath *et al.*, 1998) are isostructural and crystallize in the cubic achiral space group I −43*m*. The N_3 cluster (Atam & Müller, 1974) crystallizes in the trigonal space group P −3*c*1. The crystal structure of trimethylplatinum(IV) bromide with toluene solvent was previously reported (Massa *et al.*, 1988), which crystallizes in the lower symmetric monoclinic space group C 2/m. This can be explained by hydrophobic interactions or packing effects of the structure.

The title complex shows a distorted cubane-type structure of the tetrameric [{Pt(CH_3)$_3$Br}$_4$] unit (Fig. 1), and is disposed about a mirror plane passing through atoms Pt1, Pt2, Br1, Br2, and two methyl groups C1 and C3, parallel to the a,c plane of the unit cell, which coincide with the crystallographic mirror plane m of space group C 2/m (Fig. 2). Each Pt^{4+} ion is coordinated by three methyl groups and three μ_3-Br atoms, and the coordination geometry around respective Pt centre is distorted octahedral. Mean interatomic distances: Pt—Br 2.693 Å, Pt—C 2.028 Å, Pt···Pt 3.933 Å, Br···Br 3.668 Å. Mean bond angles: Br—Pt—Br 86.0°, Pt—Br—Pt 94.1°.

Experimental

To a solution of μ-[(1,2,5,6-η:3,4,7,8-η)-1,3,5,7-cyclooctatetraene]bis[dimethylplatinum(II)] (0.0965 g, 0.174 mmol) in CH_2Cl_2 (40 ml) and MeOH (5 ml) was added hydrobromic acid (48%; 0.0876 g, 0.519 mmol) and stirred for 4 h at room temparature. The solvent was removed *in vacuo*, the residue was washed with pentane, and dried, to give a dark yellow powder (0.0692 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from a CH_2Cl_2 solution.

Refinement

H atoms were positioned geometrically and allowed to ride on their respective carrier atoms, with C—H = 0.97 Å and with U_{iso}(H) = 1.5U_{eq}(C).

Figures

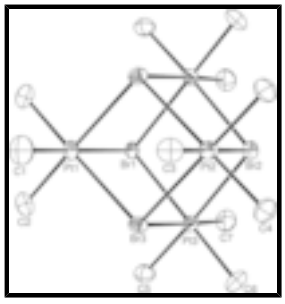

Fig. 1. The structure of the title compound, with displacement ellipsoids drawn at the 30% probability level for non-H atoms. H atoms are omitted.

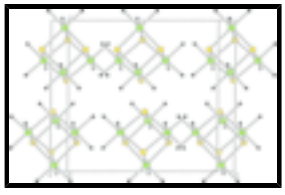

Fig. 2. View of the unit-cell contents of the title compound.

Tetra-μ$_3$-bromido-tetrakis[trimethylplatinum(IV)]

Crystal data

$[Pt_4Br_4(CH_3)_{12}]$	F_{000} = 2240
M_r = 1280.41	D_x = 3.428 Mg m^{-3}
Monoclinic, *C*2/*m*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -C 2y	Cell parameters from 2875 reflections
a = 13.8146 (12) Å	θ = 2.5–26.4º
b = 14.0793 (12) Å	μ = 28.92 mm^{-1}
c = 12.8194 (11) Å	*T* = 243 (2) K
β = 95.681 (2)º	Prism, yellow
V = 2481.1 (4) Å^3	0.15 × 0.10 × 0.08 mm
Z = 4	

Data collection

Bruker SMART 1000 CCD diffractometer	2655 independent reflections
Radiation source: fine-focus sealed tube	2189 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.035
T = 243(2) K	θ_{max} = 26.4º
φ and ω scans	θ_{min} = 1.6º
Absorption correction: multi-scan (SADABS; Bruker, 2000)	*h* = −11→17
T_{min} = 0.053, T_{max} = 0.099	*k* = −17→17
7252 measured reflections	*l* = −14→16

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters constrained
$wR(F^2) = 0.078$	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.98$	$(\Delta/\sigma)_{max} < 0.001$
2655 reflections	$\Delta\rho_{max} = 1.37$ e Å^{-3}
100 parameters	$\Delta\rho_{min} = -1.86$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pt1	0.26473 (3)	0.5000	0.04527 (4)	0.03258 (14)
Pt2	0.19786 (4)	0.5000	0.33920 (4)	0.03475 (14)
Pt3	0.42659 (2)	0.36035 (2)	0.26219 (3)	0.03335 (12)
Br1	0.45060 (8)	0.5000	0.12802 (9)	0.0289 (3)
Br2	0.38834 (9)	0.5000	0.39601 (10)	0.0345 (3)
Br3	0.23514 (6)	0.36904 (5)	0.19303 (7)	0.0321 (2)
C1	0.1250 (9)	0.5000	−0.0110 (14)	0.067 (5)
H1A	0.1200	0.5000	−0.0870	0.100*
H1B	0.0935	0.5563	0.0133	0.100*
C2	0.2882 (7)	0.3993 (7)	−0.0637 (8)	0.051 (3)
H2A	0.3563	0.3815	−0.0564	0.077*
H2B	0.2707	0.4246	−0.1334	0.077*
H2C	0.2486	0.3439	−0.0530	0.077*
C3	0.0533 (8)	0.5000	0.2947 (11)	0.045 (3)
H3A	0.0180	0.5000	0.3564	0.067*
H3B	0.0364	0.4437	0.2532	0.067*
C4	0.1728 (8)	0.4010 (7)	0.4491 (8)	0.056 (3)
H4A	0.1798	0.3379	0.4203	0.084*

H4B	0.1073	0.4087	0.4690	0.084*
H4C	0.2192	0.4092	0.5102	0.084*
C5	0.4531 (7)	0.2591 (6)	0.1556 (8)	0.051 (3)
H5A	0.4689	0.2892	0.0914	0.076*
H5B	0.3957	0.2197	0.1408	0.076*
H5C	0.5072	0.2199	0.1836	0.076*
C6	0.4019 (8)	0.2560 (7)	0.3638 (8)	0.054 (3)
H6A	0.3857	0.2836	0.4292	0.081*
H6B	0.4598	0.2171	0.3769	0.081*
H6C	0.3482	0.2168	0.3342	0.081*
C7	0.5703 (7)	0.3580 (7)	0.3175 (9)	0.055 (3)
H7A	0.5817	0.4026	0.3751	0.082*
H7B	0.6094	0.3756	0.2618	0.082*
H7C	0.5880	0.2945	0.3420	0.082*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pt1	0.0258 (3)	0.0422 (3)	0.0296 (3)	0.000	0.0016 (2)	0.000
Pt2	0.0380 (3)	0.0323 (2)	0.0361 (3)	0.000	0.0144 (2)	0.000
Pt3	0.0380 (2)	0.03095 (18)	0.0316 (2)	0.00585 (14)	0.00579 (16)	0.00379 (14)
Br1	0.0270 (6)	0.0359 (6)	0.0242 (6)	0.000	0.0049 (5)	0.000
Br2	0.0397 (7)	0.0398 (6)	0.0237 (6)	0.000	0.0027 (5)	0.000
Br3	0.0328 (5)	0.0284 (4)	0.0363 (5)	−0.0031 (3)	0.0093 (4)	−0.0019 (3)
C1	0.026 (7)	0.087 (11)	0.081 (13)	0.000	−0.021 (8)	0.000
C2	0.045 (6)	0.066 (6)	0.040 (6)	−0.004 (5)	−0.005 (5)	−0.011 (5)
C3	0.028 (7)	0.050 (8)	0.059 (10)	0.000	0.015 (7)	0.000
C4	0.076 (8)	0.051 (6)	0.043 (7)	−0.012 (5)	0.023 (6)	0.011 (5)
C5	0.059 (7)	0.039 (5)	0.055 (7)	0.008 (5)	0.008 (5)	−0.001 (5)
C6	0.065 (7)	0.050 (6)	0.050 (7)	0.001 (5)	0.011 (5)	0.024 (5)
C7	0.049 (7)	0.061 (7)	0.053 (7)	0.017 (5)	0.003 (5)	0.001 (5)

Geometric parameters (Å, °)

Pt1—C1	1.993 (13)	C1—H1A	0.9700
Pt1—C2	2.038 (9)	C1—H1B	0.9700
Pt1—C2^{i}	2.038 (9)	C2—H2A	0.9700
Pt1—Br1	2.6794 (12)	C2—H2B	0.9700
Pt1—Br3^{i}	2.7034 (9)	C2—H2C	0.9700
Pt1—Br3	2.7034 (9)	C3—H3A	0.9700
Pt2—C3	2.021 (12)	C3—H3B	0.9700
Pt2—C4^{i}	2.035 (9)	C4—H4A	0.9700
Pt2—C4	2.035 (9)	C4—H4B	0.9700
Pt2—Br2	2.6599 (13)	C4—H4C	0.9700
Pt2—Br3	2.7143 (9)	C5—H5A	0.9700
Pt2—Br3^{i}	2.7143 (9)	C5—H5B	0.9700
Pt3—C6	2.015 (8)	C5—H5C	0.9700
Pt3—C5	2.034 (9)	C6—H6A	0.9700

Pt3—C7	2.041 (10)	C6—H6B	0.9700
Pt3—Br1	2.6546 (8)	C6—H6C	0.9700
Pt3—Br2	2.6958 (9)	C7—H7A	0.9700
Pt3—Br3	2.7076 (9)	C7—H7B	0.9700
Br1—Pt3^{i}	2.6546 (8)	C7—H7C	0.9700
Br2—Pt3^{i}	2.6958 (9)		
C1—Pt1—C2	88.1 (5)	Pt3^{i}—Br1—Pt3	95.58 (4)
C1—Pt1—C2^{i}	88.1 (5)	Pt3^{i}—Br1—Pt1	94.60 (3)
C2—Pt1—C2^{i}	88.1 (6)	Pt3—Br1—Pt1	94.60 (3)
C1—Pt1—Br1	177.9 (5)	Pt2—Br2—Pt3^{i}	94.40 (3)
C2—Pt1—Br1	93.4 (3)	Pt2—Br2—Pt3	94.40 (3)
C2^{i}—Pt1—Br1	93.4 (3)	Pt3^{i}—Br2—Pt3	93.66 (4)
C1—Pt1—Br3^{i}	92.6 (4)	Pt1—Br3—Pt3	92.85 (3)
C2—Pt1—Br3^{i}	178.8 (3)	Pt1—Br3—Pt2	94.16 (3)
C2^{i}—Pt1—Br3^{i}	92.9 (3)	Pt3—Br3—Pt2	92.90 (3)
Br1—Pt1—Br3^{i}	85.87 (3)	Pt1—C1—H1A	109.5
C1—Pt1—Br3	92.6 (4)	Pt1—C1—H1B	109.5
C2—Pt1—Br3	92.9 (3)	H1A—C1—H1B	109.5
C2^{i}—Pt1—Br3	178.8 (3)	Pt1—C2—H2A	109.5
Br1—Pt1—Br3	85.87 (3)	Pt1—C2—H2B	109.5
Br3^{i}—Pt1—Br3	86.01 (4)	H2A—C2—H2B	109.5
C3—Pt2—C4^{i}	87.9 (4)	Pt1—C2—H2C	109.5
C3—Pt2—C4	87.9 (4)	H2A—C2—H2C	109.5
C4^{i}—Pt2—C4	86.4 (6)	H2B—C2—H2C	109.5
C3—Pt2—Br2	179.5 (4)	Pt2—C3—H3A	109.5
C4^{i}—Pt2—Br2	92.4 (3)	Pt2—C3—H3B	109.5
C4—Pt2—Br2	92.4 (3)	H3A—C3—H3B	109.5
C3—Pt2—Br3	93.1 (3)	Pt2—C4—H4A	109.5
C4^{i}—Pt2—Br3	178.9 (3)	Pt2—C4—H4B	109.5
C4—Pt2—Br3	94.0 (3)	H4A—C4—H4B	109.5
Br2—Pt2—Br3	86.49 (3)	Pt2—C4—H4C	109.5
C3—Pt2—Br3^{i}	93.1 (3)	H4A—C4—H4C	109.5
C4^{i}—Pt2—Br3^{i}	94.0 (3)	H4B—C4—H4C	109.5
C4—Pt2—Br3^{i}	178.9 (3)	Pt3—C5—H5A	109.5
Br2—Pt2—Br3^{i}	86.49 (3)	Pt3—C5—H5B	109.5
Br3—Pt2—Br3^{i}	85.58 (4)	H5A—C5—H5B	109.5
C6—Pt3—C5	88.6 (4)	Pt3—C5—H5C	109.5
C6—Pt3—C7	89.1 (4)	H5A—C5—H5C	109.5
C5—Pt3—C7	89.4 (4)	H5B—C5—H5C	109.5
C6—Pt3—Br1	177.4 (3)	Pt3—C6—H6A	109.5
C5—Pt3—Br1	92.4 (3)	Pt3—C6—H6B	109.5
C7—Pt3—Br1	93.3 (3)	H6A—C6—H6B	109.5
C6—Pt3—Br2	93.7 (3)	Pt3—C6—H6C	109.5
C5—Pt3—Br2	177.3 (3)	H6A—C6—H6C	109.5

C7—Pt3—Br2	92.1 (3)	H6B—C6—H6C	109.5
Br1—Pt3—Br2	85.24 (3)	Pt3—C7—H7A	109.5
C6—Pt3—Br3	91.3 (3)	Pt3—C7—H7B	109.5
C5—Pt3—Br3	92.7 (3)	H7A—C7—H7B	109.5
C7—Pt3—Br3	178.0 (3)	Pt3—C7—H7C	109.5
Br1—Pt3—Br3	86.28 (3)	H7A—C7—H7C	109.5
Br2—Pt3—Br3	85.92 (3)	H7B—C7—H7C	109.5
C5—Pt3—Br1—Pt3^{i}	−177.2 (3)	C6—Pt3—Br2—Pt3^{i}	178.4 (3)
C7—Pt3—Br1—Pt3^{i}	−87.7 (3)	C7—Pt3—Br2—Pt3^{i}	89.2 (3)
Br2—Pt3—Br1—Pt3^{i}	4.04 (4)	Br1—Pt3—Br2—Pt3^{i}	−3.97 (4)
Br3—Pt3—Br1—Pt3^{i}	90.25 (3)	Br3—Pt3—Br2—Pt3^{i}	−90.57 (3)
C5—Pt3—Br1—Pt1	87.7 (3)	C1—Pt1—Br3—Pt3	176.7 (4)
C7—Pt3—Br1—Pt1	177.2 (3)	C2—Pt1—Br3—Pt3	88.5 (3)
Br2—Pt3—Br1—Pt1	−91.04 (3)	Br1—Pt1—Br3—Pt3	−4.74 (2)
Br3—Pt3—Br1—Pt1	−4.84 (3)	Br3^{i}—Pt1—Br3—Pt3	−90.88 (3)
C2—Pt1—Br1—Pt3^{i}	176.2 (3)	C1—Pt1—Br3—Pt2	−90.2 (4)
C2^{i}—Pt1—Br1—Pt3^{i}	87.8 (3)	C2—Pt1—Br3—Pt2	−178.4 (3)
Br3^{i}—Pt1—Br1—Pt3^{i}	−4.85 (3)	Br1—Pt1—Br3—Pt2	88.37 (3)
Br3—Pt1—Br1—Pt3^{i}	−91.14 (3)	Br3^{i}—Pt1—Br3—Pt2	2.23 (4)
C2—Pt1—Br1—Pt3	−87.8 (3)	C6—Pt3—Br3—Pt1	−176.1 (3)
C2^{i}—Pt1—Br1—Pt3	−176.2 (3)	C5—Pt3—Br3—Pt1	−87.4 (3)
Br3^{i}—Pt1—Br1—Pt3	91.14 (3)	Br1—Pt3—Br3—Pt1	4.79 (3)
Br3—Pt1—Br1—Pt3	4.85 (3)	Br2—Pt3—Br3—Pt1	90.27 (3)
C4^{i}—Pt2—Br2—Pt3^{i}	−89.7 (3)	C6—Pt3—Br3—Pt2	89.6 (3)
C4—Pt2—Br2—Pt3^{i}	−176.3 (3)	C5—Pt3—Br3—Pt2	178.2 (3)
Br3—Pt2—Br2—Pt3^{i}	89.90 (3)	Br1—Pt3—Br3—Pt2	−89.53 (3)
Br3^{i}—Pt2—Br2—Pt3^{i}	4.12 (3)	Br2—Pt3—Br3—Pt2	−4.04 (3)
C4^{i}—Pt2—Br2—Pt3	176.3 (3)	C3—Pt2—Br3—Pt1	90.7 (3)
C4—Pt2—Br2—Pt3	89.7 (3)	C4—Pt2—Br3—Pt1	178.8 (3)
Br3—Pt2—Br2—Pt3	−4.12 (3)	Br2—Pt2—Br3—Pt1	−88.97 (3)
Br3^{i}—Pt2—Br2—Pt3	−89.90 (3)	Br3^{i}—Pt2—Br3—Pt1	−2.23 (4)
C6—Pt3—Br2—Pt2	−86.9 (3)	C3—Pt2—Br3—Pt3	−176.2 (3)
C7—Pt3—Br2—Pt2	−176.1 (3)	C4—Pt2—Br3—Pt3	−88.1 (3)
Br1—Pt3—Br2—Pt2	90.73 (3)	Br2—Pt2—Br3—Pt3	4.10 (3)
Br3—Pt3—Br2—Pt2	4.13 (3)	Br3^{i}—Pt2—Br3—Pt3	90.84 (3)

Symmetry codes: (i) *x*, −*y*+1, *z*.

Fig. 1

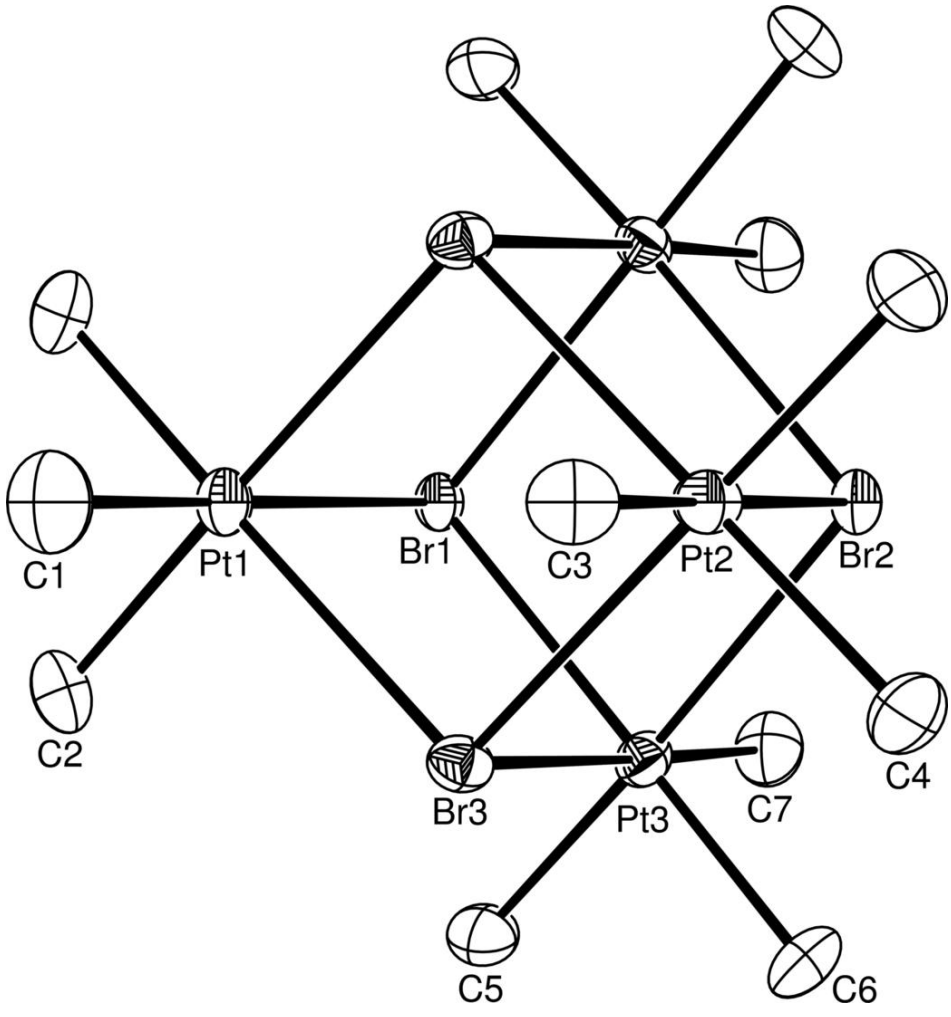

Fig. 2