

## THE X-RAY CRYSTAL STRUCTURE OF THE ORGANOPLATINUM BRIDGING DISELENIDE COMPLEX [(PtMe<sub>3</sub>I)<sub>2</sub>MeSeSeMe]

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### Summary

An X-ray crystal structure determination of the dinuclear complex [(PtMe<sub>3</sub>I)<sub>2</sub>MeSeSeMe] confirms the retention of the Se—Se bond and the presence of a bridging diselenide ligand.

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### Introduction

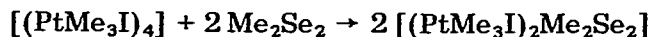
Although in the past, compounds such as MeSSMe [1] MeSeSeMe [2], Ph<sub>2</sub>PPPh<sub>2</sub> [3] and Me<sub>2</sub>AsAsMe<sub>2</sub> [4] have been extensively used as sources of the ligands MeS, MeSe, Ph<sub>2</sub>P and Me<sub>2</sub>As respectively, it has recently been established that these dinuclear compounds can act as ligands in their own right without the fission of the central bond between the donor atoms [5–8].

Invariably the presence of this type of bridging ligand causes considerable folding of the dinuclear metal complexes as evidenced to date in complexes of rhenium [5–7] and platinum [8].

We were interested to extend our investigation of this type of compound to an iodo system, in order to determine whether such a binuclear complex would survive and accommodate the longer halogen bridged bonds, whilst still retaining an Se—Se bond intact.

### Results and discussion

Dimethyldiselenide undergoes reaction with the tetranuclear trimethylplatinum iodide to produce a dinuclear product in good yield.



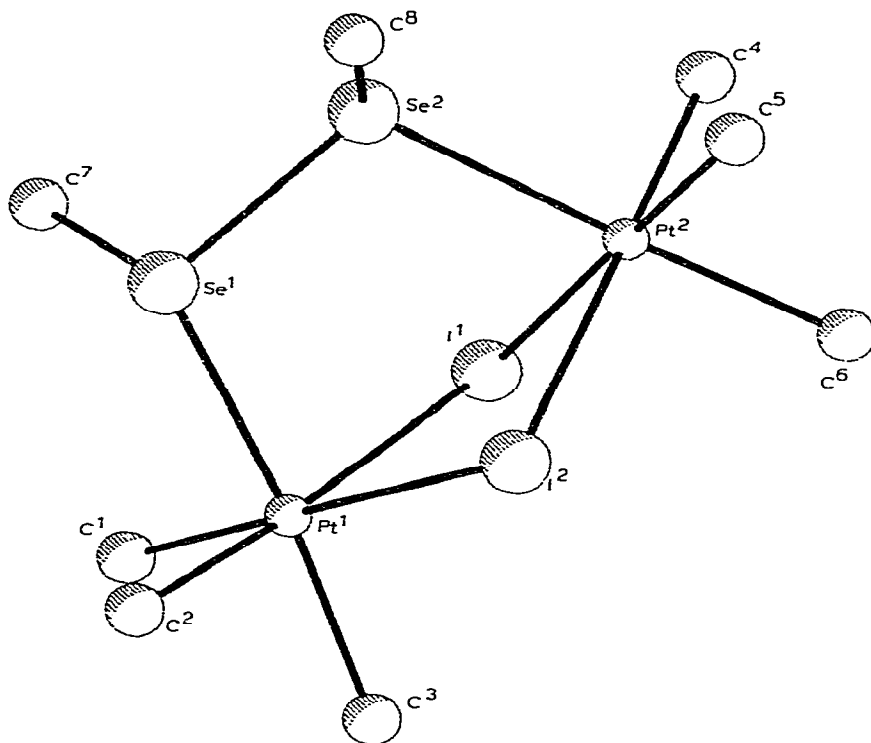


Fig. 1. The molecular structure of  $[(PtMe_3I)_2MeSeSeMe]$ .

As in the case of the corresponding bromo analogue [8], the platinum atoms in the molecule are held together by three bridging groups. Two of these are conventional halogen bridges, and the third is a diselenium bridge, as illustrated in Fig. 1.

The important change at the  $Pt_2I_2$  fragment introduced by the change from bromine to iodine is the lengthening of the platinum-platinum non-bonded distance, from 3.740 Å in the bromide to 3.901(2) Å in the iodo analogue. This is largely produced by the change in the Pt-Br to Pt-I distances of  $\sim 0.16$  Å. Interestingly the change from bromine to iodine has caused no significant increase in either the Se-Se or the Pt-Se bond lengths. The dihedral (folding) angle between the planes defined by Pt(1), I(1), I(2) and by Pt(2), I(1), I(2), is  $30.9^\circ$  compared to the corresponding angle for the bromo analogue of  $29^\circ$ .

This folding about the I-I vector allows the coordination about each platinum atom to remain essentially octahedral.

The geometry of the  $Se_2Me_2$  moiety in the bromide and iodide is virtually identical, including the torsional angles about the Se-Se vector. (C-Se-Se-C torsional angle is  $127^\circ$  for the bromo complex and  $129^\circ$  for the iodo complex).

## Experimental

The crystal used for the X-ray determination had overall dimensions of  $0.30 \times 0.30 \times 0.22$  mm and was bounded by the six intersecting planes  $[(001), (00\bar{1}),$

( $\bar{1}\bar{1}\bar{1}$ ), (11 $\bar{1}$ ) and ( $\bar{1}\bar{1}\bar{1}$ )]. Preliminary unit-cell parameters and the crystal system were determined from oscillation and Weissenberg photographs. Accurate cell parameters were derived from least square refinement of setting angles for twenty-five reflections automatically centred on the Nonius CAD-4 diffractometer. The space group  $P2_1/n$  was uniquely determined from systematic absences;  $0k0$  for  $k$  odd and  $h0l$  for  $h + l$  odd.

Crystal data:  $C_8H_{24}I_2Pt_2Se_2$ ,  $M = 922.2$ , Monoclinic,  $a$  9.942(2),  $b$  12.290(4),  $c$  15.229(4) Å,  $\beta$  105.81(2)°,  $U$  1790.4 Å<sup>3</sup>. Space group  $P2_1/n$  ( $C_{2h}^5$  No. 14),  $Z = 4$ ,  $D_c$  3.42 g cm<sup>-3</sup>.  $F(000) = 1560$ ,  $\mu(\text{Mo-K}\alpha)$  232.2 cm<sup>-1</sup>,  $\lambda(\text{Mo-K}\alpha)$  0.71069 Å.

The intensity of 3509 reflections ( $\pm h, k, l$ ;  $1.5^\circ \leq \theta \leq 25^\circ$ ) were recorded on the CAD-4 diffractometer using graphite-monochromated Mo- $K_\alpha$  radiation and  $\omega-2\theta$  scan method. Throughout the data collection, the intensities of two standard reflections were measured every one hour as a check on instrument electronics and crystal stability. No systematic change in any of the standard reflections was observed during the course of the data collection. The data was corrected for Lorentz and polarization factors, and averaged to give 3143 unique reflections. Of these, 2267 were considered observed and had intensities greater than  $2\sigma(I)$ , and were used in the structure refinement.

The positions of the two platinum atoms were obtained from the 'best' E-map computed with the automatic direct methods subroutine in the SHELX 76 programme system. These positions were also checked against a 3D Patterson map. Full-matrix least-squares refinement of these atoms ( $R = 0.24$ ) was followed by a difference synthesis from which the iodine and selenium atoms were located. Refinement with individual isotropic temperature factors gave an  $R$  value of 0.13. At this stage the data were corrected for absorption effects and refinement, as before, reduced  $R$  to 0.10. This was continued with anisotropic temperature factors for all non-hydrogen atoms of methyl groups at their idealized positions (C-H 1.08 Å, and H-C-H 109.5°), with one common isotropic thermal parameter of  $V_{\text{iso}}$  0.05 Å<sup>2</sup>, led to final values of  $R = 0.079$  and  $R_w = 0.080$ . The

TABLE 1

THE REFINED POSITIONAL PARAMETERS (Pt  $\times 10^5$ , ALL OTHERS  $\times 10^4$ ) OF NON-HYDROGEN ATOMS (with e.s.d.'s in parentheses)

Atom	x	y	z
Pt(1)	-12841(11)	16278(9)	28648(7)
Pt(2)	14583(11)	19636(9)	14764(8)
I(1)	674(2)	3230(2)	2776(1)
I(2)	333(2)	197(2)	2171(1)
Se(1)	-2589(3)	2231(2)	1245(2)
Se(2)	-977(3)	2165(3)	361(2)
C(1)	-2539(37)	2678(22)	3382(21)
C(2)	-2711(37)	452(25)	2963(26)
C(3)	-276(40)	1236(38)	4196(26)
C(4)	2201(46)	3226(31)	898(28)
C(5)	2009(44)	910(31)	537(29)
C(6)	3514(39)	1792(37)	2273(31)
C(7)	-3697(28)	974(28)	631(21)
C(8)	-1056(64)	3692(43)	-21(27)

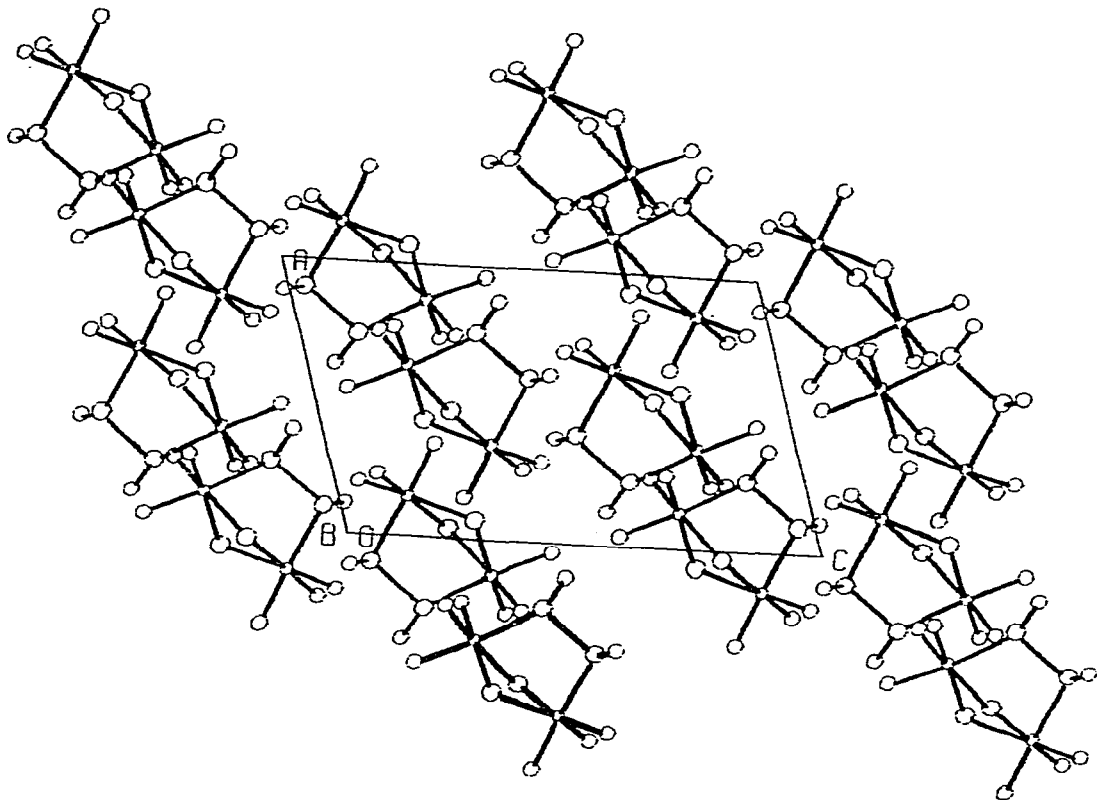


Fig. 2. Unit cell packing in the crystal of  $[(PtMe_3I)_2MeSeSeMe]$ .

weighting scheme applied was  $w = 1/[\sigma^2 |F_o| + 0.002 |F_o|^2]$ , which gave satisfactory analyses of variance with  $\sin \theta$  and  $(F_o/F_{max})^{1/2}$ .

A final difference map showed only random noise  $\leq 1.5 \text{ e}\text{\AA}^{-3}$  near the platinum atoms, but no feature of chemical significance. Neutral atom scattering factors for non-hydrogen atoms were from reference 9, and were corrected for anomalous dispersion ( $\Delta f'$ ,  $\Delta f''$ ), [10]. The scattering factor for hydrogen was taken from reference 11. The final atomic parameters are given in Table 1, along with their estimated standard deviations. Selected bond lengths and interbond angles are presented in Table 2. The unit-cell packing of the asymmetric *d*- and *l*-molecules is shown in Fig. 2. The anisotropic thermal parameters, calculated hydrogen atom positions, and the final observed and calculated structure factors are available from the authors on request.

Calculations were performed on the Queen Mary College ICL2980 and University of London CDC6600 and 7600 computers, using the programs SHELX-76 [12] for structure determination and refinement, PLUTO [13] for drawing figures, and XANADU [14] for least squares plane and torsion angle calculations.

TABLE 2

BOND LENGTHS (Å) AND BOND ANGLES (°) (with e.s.d.'s in parentheses)

Pt(1)—Pt(2)	3.901(2)	Se(1)—Se(2)	2.358(4)
Pt(1)—I(1)	2.798(2)	Pt(2)—I(1)	2.790(2)
Pt(1)—I(2)	2.778(2)	Pt(2)—I(2)	2.780(2)
Pt(1)—Se(1)	2.564(3)	Pt(2)—Se(2)	2.563(3)
Pt(1)—C(1)	2.09(3)	Pt(2)—C(4)	2.02(5)
Pt(1)—C(2)	2.06(3)	Pt(2)—C(5)	2.11(3)
Pt(1)—C(3)	2.06(3)	Pt(2)—C(6)	2.08(3)
Se(1)—C(7)	1.98(3)	Se(2)—C(8)	1.96(5)
C(1)—Pt(1)—I(1)	94.5(9)	C(4)—Pt(2)—I(1)	95(1)
C(1)—Pt(1)—I(2)	178.7(9)	C(4)—Pt(2)—I(2)	177(1)
C(1)—Pt(1)—Se(1)	89.2(9)	C(4)—Pt(2)—Se(2)	92(1)
C(1)—Pt(1)—C(3)	87(2)	C(4)—Pt(2)—C(6)	85(2)
C(1)—Pt(1)—C(2)	85(1)	C(4)—Pt(2)—C(5)	89(2)
C(2)—Pt(1)—I(1)	179(1)	C(5)—Pt(2)—I(1)	176(1)
C(2)—Pt(2)—I(2)	94(1)	C(5)—Pt(2)—I(2)	89(1)
C(2)—Pt(2)—Se(1)	95(1)	C(5)—Pt(2)—Se(2)	89(1)
C(2)—Pt(1)—C(3)	86(2)	C(5)—Pt(2)—C(6)	87(2)
C(3)—Pt(1)—I(1)	93(1)	C(6)—Pt(2)—I(1)	94(1)
C(3)—Pt(1)—I(2)	93(1)	C(6)—Pt(2)—I(2)	98(1)
C(3)—Pt(1)—Se(1)	176(1)	C(6)—Pt(2)—Se(2)	174(1)
Se(1)—Pt(1)—I(1)	85.8(1)	Se(2)—Pt(2)—I(1)	91.2(1)
Se(1)—Pt(1)—I(2)	90.6(1)	Se(2)—Pt(2)—I(2)	85.5(1)
I(1)—Pt(1)—I(2)	86.8(1)	I(1)—Pt(2)—I(2)	86.9(1)
Pt(1)—I(1)—Pt(2)	88.5(1)	Pt(1)—I(2)—Pt(2)	89.1(1)
Pt(1)—Se(1)—Se(2)	107.2(1)	Pt(2)—Se(2)—Se(1)	106.9(1)
Pt(1)—Se(1)—C(7)	107(1)	Pt(2)—Se(2)—C(8)	104(2)
C(7)—Se(1)—Se(2)	94.6(9)	C(8)—Se(2)—Se(1)	99(2)

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