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BINUCLEAR COMPLEXES OF PALLADIUM(II) AND PLATINUM(II) CONTAINING BRIDGING ETHYLSELENOLATO GROUP: X-RAY CRYSTAL STRUCTURE OF $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$

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Abstract—The reaction of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with NaSeEt in 1 : 1 and 1 : 2 stoichiometry gave $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PR_3)_2]$ and $[M_2Cl_2(\mu\text{-}SeEt)_2(PR_3)_2]$ (M = Pd or Pt; $PR_3 = PEt_3$, PBu_3, PMe_2Ph or $PMePh_2$), respectively. These complexes were characterized by elemental analysis and NMR data (^1H and ^{31}P). The mixed chloro/ethylselenolato bridged complexes adopt a *cis* configuration with phosphine *trans* to the bridging chloride. The molecular structure of $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$ has been determined by single crystal X-ray diffraction. The complex has a planar four-membered "Pt_2Se_2" bridge.

The chemistry of transition metal complexes with chalcogen ligands is of broad research interest[1] and is currently expanding at a rapid rate. Besides diverse structural possibilities, they have been used as precursors for the preparation of new solid-state materials,[2] industrial catalysts (e.g. hydrodesulphurization[3]) and models for enzymatic reactions in biological systems. The chemistry of binuclear palladium(II) and platinum(II) complexes of the type $[M_2X_2(\mu\text{-}Y)(\mu\text{-}ER')(PR_3)_2]$ (Y = Cl or ER′) has been dominated by molecules containing bridging thiolato (E = S) groups.[4-23] Subtle variation in the nature of X, Y, R′ (alkyl or aryl) and PR_3 leads to diversity in the structural features and also influences chemical reactivity of such complexes. Complexes with heavier chalcogens (E = Se or Te) are rare.[24] Recently, a few complexes with the SePh group were reported by us[23,25] and others,[26] but in no case was the structural features of these complexes investigated. This has motivated us to explore the chemistry of binuclear palladium and platinum complexes with heavier organochalcogenide (E = Se or Te) bridges with the hope of isolating new structure types. In this paper we report studies aimed at synthesis and

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structural features of alkylselenolato-bridged binuclear palladium and platinum complexes.

RESULTS AND DISCUSSION

The reaction of $[M_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$ with NaSeEt prepared by reductive cleavage of the Se—Se bond in Se_2Et_2 with sodium borohydride, in 1 : 1 and 1 : 2 stoichiometry, afforded ethylselenolato-bridged complexes of the types $[M_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PR_3)_2]$ and $[M_2Cl_2(\mu\text{-}SeEt)_2(PR_3)_2]$ (M = Pd or Pt; PR_3 = PEt_3, PBu_3, PMe_2Ph or $PMePh_2$), respectively. Platinum complexes are cream coloured while palladium derivatives are yellow in colour.

The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ and the resulting data are summarized in Table 1. NMR data are consistent with the $[M_2Cl_2(\mu\text{-}Y)(\mu\text{-}SeEt)(PR_3)_2]$ (M = Pd or Pt; Y = Cl or SeEt) arrangement. The bis(ethylselenolato)-bridged complexes displayed one or two resonances in the ^{31}P NMR spectra attributable to a *cis*/*trans* or a mixture of these isomers, respectively. Resonances for platinum complexes were flanked by the ^{195}Pt isotope, with a $^1J(^{195}Pt\text{–}^{31}P)$ value of ~3200 Hz. The ^1H NMR spectra exhibited two or three sets of resonances for SeEt protons assignable to *cis* and a mixture of *cis* and *trans* isomers, respectively. The spectra of mixed chloro/ethylselenolato-bridged complexes were interpreted in terms of a *cis* configuration with phosphine ligands *trans* to bridging chloride.[16] The complexes containing dimethylphenylphosphine displayed two doublets for the PMe protons, indicating non-equivalence of the methyl groups on phosphine.

Structure of $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$

An ORTEP plot with the numbering scheme of the molecular structure of $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$ is shown in Fig. 1. Selected bond distances and angles are given in Table 2. The complex is dimeric with two square planar platinum atoms joined together by two ethylselenolato groups. The molecule has a *sym trans* configuration with a nearly planar four-membered Pt_2Se_2 ring. This is in contrast to the alkylthiolato-bridged complexes, which have non-planar Pt_2S_2 rings.[8,12,13,21] To minimize crowding, the ethyl groups of the selenolato ligands point away from the phosphine ethyl groups; consequently, the μ-SeEt groups adopt an *anti* conformation. Crowding is further minimized by the opening of P—Pt—Se angles [97.1(2), 96.2(2)°] from the ideal value of 90°.

The Pt—Se distances are sensitive to the *trans* influence of the ligands *trans* to the SeEt group. Accordingly, the Pt—Se distances *trans* to the phosphine ligands [2.466(3) and 2.482(3) Å] are longer than those *trans* to terminal chloride [2.394(3) and 2.408(3) Å]. The Pt—Se distances are in agreement with those reported for $[PtCl_4\{o\text{-}C_6H_4(SeMe)_2\}]$ [2.436 Å (av)][27] and $[(CO)_6Fe_2(\mu\text{-}Se)_2Pt(PPh_3)_2]$ [2.45 Å (av)].[28] The Pt—Cl [2.353(8), 2.308(8) Å],[8,22] Pt—P,[8,22] P—C[8,22] and Se—C[27,29] distances are in agreement with the reported values.

The Se—Pt—Se angles [83.4(1), 82.8(1)°] are significantly smaller than the ideal value, indicating strain in the four-membered ring. Unlike thiolato-bridged complexes,[8,12,13] the Pt—Se—Pt angles [96.8(1) and 96.9(1)°] are essentially identical and are much larger than the corresponding Pt—S—Pt angle in an analogous alkylthiolato-bridged complex $[Pt_2Cl_2(\mu\text{-}SEt)_2(PR_3)_2]$[85.1(2), 89.7(2)°].[8] Although a wide variation in the angle of the bridging thiolato complexes has been reported with different metal ions, opening of the Pt—Se—Pt angle in the present case may be attributed to the larger size of the selenium atom.

EXPERIMENTAL

$[Pd_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$,[30] $[Pt_2Cl_2(\mu\text{-}Cl)_2(PR_3)_2]$[30] and Se_2Et_2[31] were prepared according to the literature methods. Reactions were carried out under a nitrogen atmosphere in dry and distilled analytical grade solvents. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker AMX-500 spectrometer in a 5 mm NMR tube. ^1H NMR chemical shifts are referred to the internal chloroform peak (δ 7.26 ppm), while ^{31}P NMR shifts are relative to external 85% H_3PO_4. Microanalyses of the complexes were carried out in the Analytical Chemistry Division of the Bhabha Atomic Research Centre.

Preparation of $[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PEt_3)_2]$

To a methanol solution (5 cm^3) of Se_2Et_2 (17 mg, 0.078 mmol) a dilute methanolic solution of $NaBH_4$ was added with vigorous stirring under nitrogen. Addition of the $NaBH_4$ solution was stopped when a colourless solution of NaSeEt was obtained. To this a dichloromethane (10 cm^3) solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (120 mg, 0.156 mmol) was added and stirred for 3 h. The solvents were stripped off *in vacuo*. The residue was extracted with dichloromethane and recrystallized from dichloromethane–ethanol as a pale yellow crystalline solid (114 mg, 87%). The other chloro/ethylselenolato-bridged complexes of palladium and platinum were prepared in analogous manner and the pertinent data are given in Table 3.

Table 1. ^1H and ^{31}P NMR data for $[M_2Cl_2(\mu\text{-}Y)(\mu\text{-}SeEt)(PR_3)_2]$ (M = Pd or Pt; Y = Cl or SeEt) in $CDCl_3$

Complex	$^{31}P\{^1H\}$ NMR data		^1H NMR data
	δ (ppm)	$^1J(^{195}Pt\text{–}^{31}P)$ (Hz)	
$[Pd_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$	10.3	—	1.20 (m, 18H, P—C—CH_3); 1.47 (t, 7.5 Hz, 3H, Se—C—CH_3); 1.61 (t, 7.5 Hz, 3H, Se—C—CH_3); 1.84–2.12 (m, 12H, PCH_2—); 2.72 (q, 7.5 Hz, $SeCH_2$); 3.08 (m, $SeCH_2$—); 3.21 (q, 7.5 Hz, $SeCH_2$—) (in 1 : 1 : 1) (*cis* + *trans*).
$[Pd_2Cl_2(\mu\text{-}SeEt)_2(PBu_3)_2]$	28.7	—	0.94 (t, 7.2 Hz, 18H, P—C—C—C—CH_3); 1.41–1.61 (m, PC—CH_2CH_2— + SeC—CH_3); 1.84–1.89 (m, PCH_2—); 2.69 (q, 7.5 Hz, $SeCH_2$—); 3.05 (m, $SeCH_2$—) (*cis*).
$[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$	5.4 4.4	3155 (*trans*) 3150 (*cis*)	1.17 (m, 18H, PC—CH_3); 1.38 (t, 7.5 Hz, Se—C—CH_3); 1.63 (t, 7.5 Hz, $SeCCH_3$); 1.76 (m, $SeCH_2$—); 1.89 (m, 12H, PCH_2—); 2.74 (m, $SeCH_2$—); 3.23 (m, $SeCH_2$—)
$[Pt_2Cl_2(\mu\text{-}SeEt)_2(PMe_2Ph)_2]$	−18.4	3199 (*cis*)	0.94 (t, 7.5 Hz, SeC—CH_3); 1.63 (t, 7.5 Hz, SeC—CH_3); 1.77 (d, 10.7 Hz, PMe_2); 1.82 (d, 10.7 Hz, PMe_2); 2.30 (m, $SeCH_2$—); 3.26 (m, $SeCH_2$); 7.39–7.65 (m, Ph).
$[Pt_2Cl_2(\mu\text{-}SeEt)_2(PMePh_2)_2]$	−3.8	3270 (*cis*)	0.57 (t, 7.5 Hz, Se—C—CH_3); 1.73 (t, 7.5 Hz, Se—CCH_3); 1.89 (q, 7.5 Hz, $SeCH_2$—); 2.14 (d, 10.5 Hz, PMe); 3.37 (m, br, $SeCH_2$—); 7.28–7.71 (m, Ph).
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PEt_3)_2]$	37.3	—	1.23 (m, 18H, P—C—CH_3); 1.61 (t, 7.5 Hz, SeC—CH_3); 2.02 (m, 12H, PCH_2—); 3.20 (m, 2H, $SeCH_2$—).
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PBu_3)_2]$	28.9	—	1.23 (m, 18H, P—C—C—C—CH_3); 1.61 (t, 7.5 Hz, SeC—CH_3); 2.02 (m, $PCH_2CH_2CH_2$—); 3.20 (m, $SeCH_2$—).
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMe_2Ph)_2]$	7.4	—	1.14 (t, 7.4 Hz, $SeCCH_3$); 1.88 (d, 12.2 Hz, PMe); 1.97 (d, 12.2 Hz, PMe); 2.65 (q, 7.5 Hz, $SeCH_2$—); 7.43–7.65 (m, Ph).
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMePh_2)_2]$	8.6	—	0.86 (t, 7.5 Hz, SeC—CH_3); 2.23 (d, 12.2 Hz, PMe); 2.32 (q, 7.5 Hz, $SeCH_2$—); 7.31–7.61 (m, Ph).
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PEt_3)_2]$	6.3	3971	1.12 (m, 18H, PC—CH_3); 1.19 (t, Se—C—CH_3); 1.89 (m, 12H, PCH_2—); 3.02 (q, 7.5 Hz, $SeCH_2$—).
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PBu_3)_2]$	−2.1	3935	0.96 (t, 7.3 Hz, P—C—C—C—CH_3); 1.46 (m); 1.57 (m); 1.90 (m) (PCH_2 + Se—C—CH_3); 3.07 (q, 7.5 Hz, $SeCH_2$—).
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMe_2Ph)_2]$	−21.0	4043	1.11 (t, 7.5 Hz, SeC—CH_3); 1.86 (d, 11.8 Hz, PMe); 1.91 (d, 11.8 Hz, PMe); 2.54 (q, 7.5 Hz); 7.40–7.68 (m, Ph).
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMePh_2)_2]$	—	—	0.82 (t, 7.5 Hz, SeC—CH_3); 2.00 (br, $SeCH_2$—); 2.20 (d, 11.5 Hz, PMe); 7.33–7.74 (m, Ph)

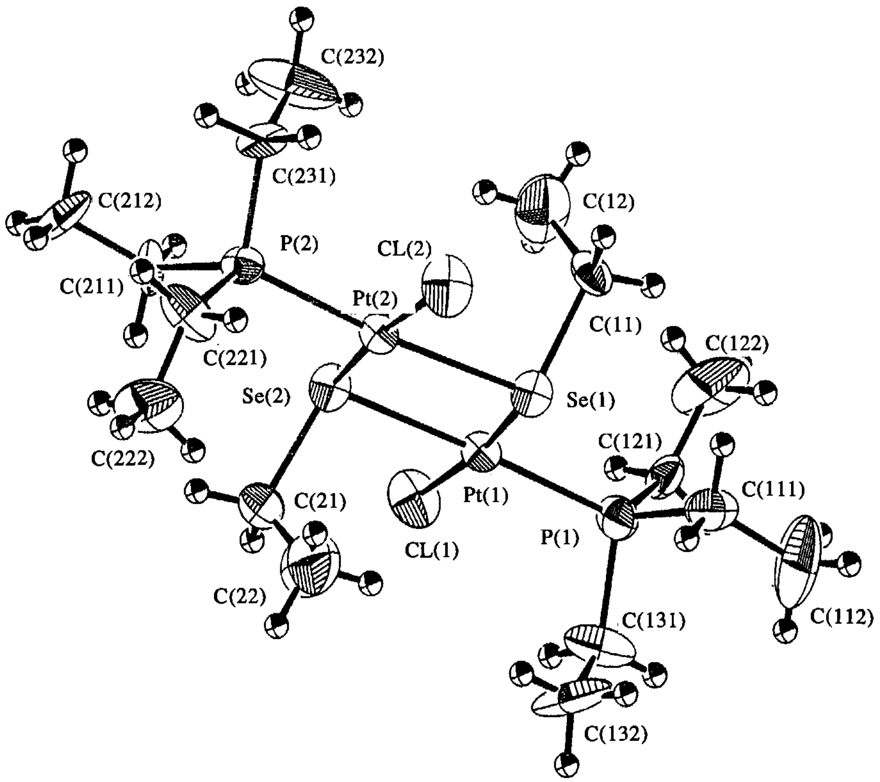

Fig. 1. ORTEP diagram of $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$.

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.s of $[\{Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]^a$

Pt(1)—Se(1)	2.394(3)	Se(1)—C(11)	1.96(3)
Pt(1)—Se(2)	2.466(3)	Se(2)—C(21)	1.99(3)
Pt(1)—C(11)	2.353(8)	P(1)—C(111)	1.84(3)
Pt(1)—P(1)	2.274(9)	P(1)—C(121)	1.84(3)
Pt(2)—Se(1)	2.482(3)	P(1)—C(131)	1.85(4)
Pt(2)—Se(2)	2.408(3)	P(2)—C(211)	1.78(3)
Pt(2)—C(12)	2.308(8)	P(2)—C(221)	1.85(3)
Pt(2)—P(2)	2.250(8)	P(2)—C(231)	1.84(3)
Se(1)—Pt(1)—Se(2)	83.4(1)	Pt(1)—P(1)—C(121)	116(1)
Se(1)—Pt(1)—Cl(1)	172.9(3)	Pt(1)—P(1)—C(131)	109(1)
Se(1)—Pt(1)—P(1)	97.1(2)	Pt(2)—P(2)—C(211)	118(1)
Cl(1)—Pt(1)—P(1)	89.9(3)	Pt(2)—P(2)—C(221)	115(1)
Se(2)—Pt(1)—Cl(1)	89.6(3)	Pt(2)—P(2)—C(231)	109(1)
Se(2)—Pt(1)—P(1)	177.4(2)	Se(1)—C(11)—C(12)	118(2)
Se(1)—Pt(2)—Se(2)	82.8(1)	Se(2)—C(21)—C(22)	110(2)
Se(1)—Pt(2)—Cl(2)	89.0(2)	C(111)—P(1)—C(121)	108(2)
Se(1)—Pt(2)—P(2)	174.0(2)	C(111)—P(1)—C(131)	106(2)
Se(2)—Pt(2)—Cl(2)	171.7(3)	C(121)—P(1)—C(131)	101(2)
Se(2)—Pt(2)—P(2)	96.2(2)	C(211)—P(2)—C(221)	103(1)
Cl(2)—Pt(2)—P(2)	91.8(3)	C(211)—P(2)—C(231)	105(2)
Pt(1)—Se(1)—Pt(2)	96.8(1)	C(221)—P(2)—C(231)	106(2)
Pt(1)—Se(2)—Pt(2)	96.9(1)	P(1)—C(111)—C(112)	113(3)
Pt(1)—Se(1)—C(11)	102.8(9)	P(1)—C(121)—C(122)	112(3)
Pt(2)—Se(1)—C(11)	100.3(8)	P(1)—C(131)—C(132)	112(3)
Pt(1)—Se(2)—C(21)	99.9(9)	P(2)—C(211)—C(212)	117(2)
Pt(2)—Se(2)—C(21)	106(1)	P(2)—C(221)—C(222)	116(3)
Pt(1)—P(1)—C(111)	115(1)	P(2)—C(231)—C(232)	116(2)

[a] Average C—C of ethyl groups = 1.47 Å.

Table 3. Physical and analytical data for $[M_2Cl_2(\mu\text{-}Y)(\mu\text{-}SeEt)(PR_3)_2]$ (Y = Cl or SeEt)

Complex	Solvent of recrystallization (% yield)	M.p. (°C)	Analysis, found (calc.)	
			C	H
$[Pd_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$	CH_2Cl_2–EtOH	175 (d)	25.1	5.4
	(58)		(26.1)	(5.5)
$[Pd_2Cl_2(\mu\text{-}SeEt)_2(PBu_3)_2]$	EtOH	122	36.2	6.9
	(60)		(37.2)	(7.1)
$[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$	CH_2Cl_2–EtOH	175	20.8	4.2
	(72)		(21.0)	(4.4)
$[Pt_2Cl_2(\mu\text{-}SeEt)_2(PMe_2Ph)_2]$	CH_2Cl_2–EtOH	162	24.9	3.3
	(75)		(25.2)	(3.4)
$[Pt_2Cl_2(\mu\text{-}SeEt)_2(PMePh_2)_2]$	CH_2Cl_2–EtOH	240	33.3	3.3
	(70)		(33.4)	(3.4)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PEt_3)_2]$	CH_2Cl_2–EtOH	210 (d)	25.5	5.2
	(75)		(25.3)	(5.3)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PBu_3)_2]$	EtOH	130	37.3	7.0
	(80)		(37.5)	(7.1)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMe_2Ph)_2]$	CH_2Cl_2–EtOH	185 (d)	31.2	3.6
	(70)		(30.7)	(3.9)
$[Pd_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMePh_2)_2]$	CH_2Cl_2–EtOH	180 (d)	40.2	3.7
	(80)		(40.6)	(3.8)
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PEt_3)_2]$	CH_2Cl_2–EtOH	225 (d)	20.0	4.2
	(87)		(20.0)	(4.2)
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PBu_3)_2]$	EtOH	115	31.0	5.9
	(85)		(30.9)	(5.9)
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMe_2Ph)_2]$	CH_2Cl_2–EtOH	160–161	24.6	3.1
	(65)		(24.5)	(3.1)
$[Pt_2Cl_2(\mu\text{-}Cl)(\mu\text{-}SeEt)(PMePh_2)_2]$	CH_2Cl_2–EtOH	190 (d)	32.6	3.2
	(70)		(33.5)	(3.1)

Preparation of $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$

A dichloromethane (15 cm^3) solution of $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ (120 mg, 0.156 mmol) was added to a vigorously stirred solution of NaSeEt [prepared from Se_2Et_2 (45 mg, 0.208 mmol) with $NaBH_4$ in methanol (10 cm^3)] under a nitrogen atmosphere. The whole solution was stirred for 4 h. The solvents were removed under vacuum. The residue was extracted with dichloromethane, filtered and dried. It was then recrystallized from dichloromethane–ethanol as a cream coloured crystalline solid which was filtered through a fritz, washed with ethanol and dried *in vacuo* (103 mg, 72%). Other bis(ethylselenolato)-bridged complexes of palladium and platinum were prepared similarly.

Crystallography

All measurements were made at 23±1°C on a Rigaku AFC65 diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). Crystallographic data, together with data collection and structure refinement details, are given in Table 4. All the data were corrected for Lorentz and polarization effects. The structure was solved by a combination of the Patterson method and direct methods,[32] and refined by full-matrix least-squares with non-hydrogen atoms refined anisotropically. The final cycle of full matrix least-squares refinement converged with unweighted and weighted agreement factors of:

$$R = \Sigma||F_0|-|F_c||/\Sigma|F_0| = 0.045$$

$$R' = [\Sigma(|F_0|-|F_c|)^2/\Sigma wF_0{}^2]^{1/2} = 0.048$$

for $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. Plots of $\Sigma w(|F_0|-|F_c|)^2$ versus $|F_0|$, reflection order in data collection $\sin\theta$, λ and various classes of indices showed no unusual trends. The maximum and minimum excursions in the final difference Fourier map were 1.56 and -3.22 e $Å^{-3}$, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[33] Anomalous dispersion effects

Table 4. Crystal data and refinement details for $[Pt_2Cl_2(\mu\text{-}SeEt)_2(PEt_3)_2]$

Formula	$C_{16}H_{40}Se_2P_2Cl_2Pt_2$
Molecular weight	913.45
Crystal system	Orthorhombic
Space group	$P_{ca}2_1$ (no. 29)
a (Å)	21.231(4)
b (Å)	8.093(2)
c (Å)	15.366(2)
V (Å^3)	2640
Z	4
D_c (g cm^{-3})	2.298
F(000)	1696
μ (cm^{-1})	137.54
Scan type	ω
Scan rate (in ω/° min^{-1})	8.0 (two rescans)
Scan width (°)	$0.98+0.30 \tan\theta$
2θ max (°)	50.0
Unique no. of reflections	2678
No. of observations with $I \geqslant 3.00\sigma(I)$	1827
No. of variables	217
Reflection/parameter ratio	8.42
Residuals R, R'	0.045, 0.048
Goodness of fit indicator	1.61
Maximum shift/error in final cycle	0.70

were included in F_{calc}.[34] The values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[35] All calculations were performed using the TEXSAN[36] crystallographic software package of the Molecular Structure Corporation. The ORTEP[37] plot of the molecule is illustrated in Fig. 1.

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