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Monomeric Selenopalladates and Selenoplatinates

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The compounds $[\mathrm{NEt_4}]_5[2\mathrm{Pd(Se_4)_2}\cdot{}^1/_2\mathrm{Pd(Se_5)_2}]$, α-$[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_3}]\cdot\mathrm{DMF}$, and β-$[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_3}]$ have been prepared from the reaction of the appropriate metal xanthate with $\mathrm{Li_2Se}$ and Se in DMF. The $[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_2}]$ compound was isolated from the reduction of α-$[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_3}]\cdot\mathrm{DMF}$ with $\mathrm{LiBEt_3H}$ in DMF. In $[\mathrm{NEt_4}]_5[2\mathrm{Pd(Se_4)_2}\cdot{}^1/_2\mathrm{Pd(Se_5)_2}]$ the two independent $[\mathrm{Pd(Se_4)_2}]^{2-}$ anions have a Pd atom chelated by two $\mathrm{Se_4}^{2-}$ chains in slightly distorted square-planar coordination. In the $[\mathrm{Pd(Se_5)}]^{2-}$ anion the Pd center is in a square-planar coordination being chelated by two $\mathrm{Se_5}^{2-}$ ligands. Both the α- and β-$[\mathrm{Pt(Se_4)_3}]^{2-}$ anions have an octahedral Pt atom chelated by three $\mathrm{Se_4}^{2-}$ chains. The conformation of the chains around the Pt atom is $\Delta\lambda\lambda\delta$ (or $\Lambda\delta\delta\lambda$) in the α-anion and $\Delta\lambda\delta\delta$ (or $\Lambda\delta\lambda\lambda$) in the β-anion. The $[\mathrm{Pt(Se_4)_2}]^{2-}$ anion is similar in geometry to the two $[\mathrm{Pd(Se_4)_2}]^{2-}$ anions. $^{77}\mathrm{Se}$ NMR resonances for these ions (δ, ppm): $[\mathrm{Pd(Se_4)_2}]^{2-}$, 758, 893; $[\mathrm{Pd(Se_5)_2}]^{2-}$, 509, 647, 875; $[\mathrm{Pt(Se_4)_3}]^{2-}$, 680, 790; $[\mathrm{Pt(Se_4)_2}]^{2-}$, 642, 747. The Pt species exhibit the following $^{195}\mathrm{Pt}$ NMR resonances (δ, ppm): $[\mathrm{Pt(Se_4)_3}]^{2-}$, –4217; $[\mathrm{Pt(Se_4)_2}]^{2-}$, –4568. Unit cell data: $[\mathrm{NEt_4}]_5[2\mathrm{Pd(Se_4)_2}\cdot{}^1/_2\mathrm{Pd(Se_5)_2}]$, space group C_{2h}^5-$P2_1/n$, $a = 26.965(5)$ Å, $b = 10.543(2)$ Å, $c = 26.580(5)$ Å, $\beta = 106.62(3)^\circ$, $V = 7241(2)$ Å^3, $Z = 4$ (–163 °C); α-$[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_3}]\cdot\mathrm{DMF}$, space group C_i^1-$P\bar{1}$, $a = 10.066(2)$ Å, $b = 16.383(3)$ Å, $c = 17.253(3)$ Å, $\alpha = 83.08(3)^\circ$, $\beta = 86.41(3)^\circ$, $\gamma = 86.24(3)^\circ$, $V = 2814(1)$ Å^3, $Z = 2$ (–163 °C); β-$[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_3}]$, space group C_{2h}^5-$P2_1/c$, $a = 13.167(3)$ Å, $b = 11.511(2)$ Å, $c = 34.428(7)$ Å, $\beta = 98.45(3)^\circ$, $V = 5161(2)$ Å^3, $Z = 4$ (–163 °C); $[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_2}]$, space group C_2^2-$P2_1$, $a = 10.974(2)$ Å, $b = 15.314(3)$ Å, $c = 14.180(3)$ Å, $\beta = 92.03(3)^\circ$, $V = 2382(1)$ Å^3, $Z = 2$ (–163 °C).

Introduction

The first polysulfidometalates were synthesized in the early 1900s and included $[\mathrm{NH_4}]_2[\mathrm{Pt(S_5)_3}]$[1] and $[\mathrm{NH_4}]_2[\mathrm{PdS_{11}}]$.[2] The former contains the completely inorganic chiral anion $[\mathrm{Pt(S_5)_3}]^{2-}$,[3] and the latter, a polymeric palladium–sulfur network.[4] The last 25 years has seen a renewed interest in the chemistry of soluble polysulfide complexes,[5,6] while in the past 5 years the chemistry of soluble polyselenide and polytelluride complexes has been the object of intense investigation.[7–9] The Ni triad has continued to play a significant role in the elucidation of the soluble chemistry of the chalcogenides. Within that triad there are known 17 anionic polychalcogenide complexes with 12 different structural motifs. The most common species is the monomeric $[\mathrm{M(Q_4)_2}]^{2-}$ anion (Q = S, M = Ni,[10,11] Pd;[10] Q = Se, M = Ni,[12–14] Pd,[13,15] Pt;[13,15] Q = Te, M = Pd[16,17]), but several other monomers are known, including $[\mathrm{Pt(S_5)_2}]^{2-}$,[18,19] $[\mathrm{Pt(S_5)_3}]^{2-}$,[1,3,18,20–22] $[\mathrm{Pt(S_6)_2(S_5)}]^{2-}$,[23] $[\mathrm{Pt(S_6)_3}]^{2-}$,[24] and $[\mathrm{Pt(Se_4)_3}]^{2-}$.[25] There also exist multiple-metal species, such as the dimeric $[\mathrm{Pd_2(S_7)_4}]^{4-}$ ion[26] and the remarkable cubanes $[\mathrm{Ni_4Se_4(Se_3)_5(Se_4)}]^{4-}$,[27,28] $[\mathrm{Ni_4Te_4(Te_2)_2(Te_3)_4}]^{4-}$,[28] and $[\mathrm{Pt_4Te_4(Te_3)_6}]^{4-}$.[29] And, finally, the fascinating polymeric materials "$[\mathrm{PdS_{11}}]^{2-}$"[2,4] and "$[\mathrm{PdSe_{10}}]^{2-}$"[30] have been synthesized.

Here we report the synthesis and characterization of two new selenides $[\mathrm{NEt_4}]_5[2\mathrm{Pd(Se_4)_2}\cdot{}^1/_2\mathrm{Pd(Se_5)_2}]$ and β-$[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_3}]$, and we provide additional details on $[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_2}]$[13,15] and α-$[\mathrm{PPh_4}]_2[\mathrm{Pt(Se_4)_3}]\cdot\mathrm{DMF}$.[25]

Experimental Section

Syntheses. All manipulations were carried out under $\mathrm{N_2}$ with the use of standard Schlenk-line techniques. Solvents were used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Oneida Research Services, Whitesboro, NY. $^{77}\mathrm{Se}$ and $^{195}\mathrm{Pt}$ chemical shifts are referenced to $\mathrm{Me_2Se}$ and $\mathrm{Na_2PtCl_6}$, respectively. Experimental details on $^{77}\mathrm{Se}$ NMR spectroscopy have been published previously;[31] $^{195}\mathrm{Pt}$ NMR resonances were measured with a 2-s delay time and a pulse width of 20 μs for a 90° pulse angle. $\mathrm{Pd(xan)_2}$ and $\mathrm{Pt(xan)_2}$ (xan = $\mathrm{S_2COEt}$) were prepared by published methods.[32] $\mathrm{Li_2Se}$ was

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Table I. Crystallographic Details

compd	[NEt$_4$]$_5$[Pd$_{2.5}$Se$_{21}$] (**1**)	α-[PPh$_4$]$_2$[PtSe$_{12}$]·DMF (**2**)	β-[PPh$_4$]$_2$[PtSe$_{12}$] (**3**)	[PPh$_4$]$_2$[PtSe$_8$] (**4**)
formula	$C_{40}H_{100}N_5Pd_{2.5}Se_{21}$	$C_{51}H_{47}NOP_2PtSe_{12}$	$C_{48}H_{40}P_2PtSe_{12}$	$C_{48}H_{40}P_2PtSe_8$
fw	2575	1894	1821	1506
a, Å	26.965(5)	10.066(2)	13.167(3)	10.974(2)
b, Å	10.543(2)	16.383(3)	11.511(2)	15.314(3)
c, Å	26.580(5)	17.253(3)	34.428(7)	14.180(3)
α, deg.	90.00	83.08(3)	90.00	90.00
β, deg.	106.62(3)	86.41(3)	98.45(3)	92.03(3)
γ, deg.	90.00	86.24(3)	90.00	90.00
V, Å^3	7241(2)	2814(1)	5161(2)	2382(1)
Z	4	2	4	2
d(calcd), g/cm^3	2.362	2.236	2.344	2.099
space group	C_{2h}^5-$P2_1/n$	C_i^1-$P\bar{1}$	C_{2h}^5-$P2_1/c$	C_2^2-$P2_1$
t, °C	−163	−163	−163	−163
λ, Å	0.7093 (Mo Kα_1)	1.5406 (Cu Kα_1)	0.7093 (Mo Kα_1)	0.7093(Mo Kα_1)
μ, cm^{-1}	124.8	149.0	112.2	91.3
transm coeff	0.166–0.336	0.054–0.263	0.069–0.227	0.127–0.317
$R(F_o)$ ($F_o^2 > 2\sigma(F_o^2)$)	0.142	0.046	0.062	0.052
$R_w(F_o^2)$ (all data)	0.332	0.115	0.108	0.082

prepared by the reaction of stoichiometric amounts of Li and gray Se in liquid ammonia.

Preparation of [NEt$_4$]$_5$[2Pd(Se$_4$)$_2$·$^1/_2$Pd(Se$_5$)$_2$] (1). Li_2Se (279 mg, 3 mmol), gray Se (948 mg, 12 mmol), and NEt$_4$Cl (331 mg, 2 mmol) dissolved in DMF (20 mL) were added to a solution of Pd(xan)$_2$ (348 mg, 1 mmol) in DMF (20 mL). The mixture was stirred for 1 h and then filtered. Ether (60 mL) was layered on top of the filtrate, and the solution was cooled to −40 °C. Brown-red crystals of **1** formed over a period of 1 week (638 mg, 62% yield based on Pd). Anal. Calc for $C_{40}H_{100}N_5Pd_{2.5}Se_{21}$: C, 18.65; H, 3.91; N, 2.72; Pd, 10.33; Se, 64.38. Found: C, 19.45; H, 4.16; N, 2.74; Pd, 10.23; Se, 63.10. ^{77}Se NMR (DMF, δ): 509, 647, 758, 875, 893 ppm.

Synthesis of α-[PPh$_4$]$_2$[Pt(Se$_4$)$_3$]·DMF (2).[33] Li_2Se (279 mg, 3 mmol), gray Se (948 mg, 12 mmol), and PPh$_4$Cl (750 mg, 2 mmol) dissolved in DMF (30 mL) were added to a solution of Pt(xan)$_2$ (437 mg, 1 mmol) in DMF (10 mL). The mixture was stirred for 1 h and then filtered. Ether (60 mL) was layered on top of the filtrate, and the solution was cooled to −40 °C. Brown crystals of **2** formed over 1 week (1413 mg, 75% yield). Anal. Calc for $C_{51}H_{47}NP_2PtSe_{12}$: C, 32.3; H, 2.5; P, 3.3; Pt, 10.3; Se, 50.0. Found: C, 31.8; H, 2.4; P, 3.0; Pt, 9.9; Se, 48.2. ^{77}Se NMR (DMF, δ): 680, 790 ppm. ^{195}Pt NMR (DMF, δ): −4217 ppm.

Synthesis of β-[PPh$_4$]$_2$[Pt(Se$_4$)$_3$] (3).[33] Additional ether (20 mL) was added to the filtrate from **2**. A mixture of crystals of **2** and **3** (30 mg) was produced over 2 days.

Synthesis of [PPh$_4$]$_2$[Pt(Se$_4$)$_2$] (4). A solution of 1.0 M LiBEt$_3$H in THF (2 mL, 0.2 mmol) was added to **2** (189 mg, 0.1 mmol) dissolved in DMF (10 mL). The mixture was stirred for 10 min and then filtered. Ether was added until the solution was cloudy. Red crystals of **4** formed overnight (108 mg, 72% yield). Anal. Calc for $C_{48}H_{40}P_2PtSe_8$: C, 38.29, H, 2.68; P, 4.11; Pt, 12.96; Se, 41.96. Found: C, 38.03; H, 2.55; P, 3.90; Pt, 12.56; Se, 40.27. ^{77}Se NMR (DMF, δ): 642, 747 ppm. ^{195}Pt NMR (DMF, δ): −4568 ppm.

Table II. Anion Atomic Positions and Equivalent Isotropic Thermal Parameters for [NEt$_4$]$_5$[2Pd(Se$_4$)$_2$·$^1/_2$Pd(Se$_5$)$_2$] (**1**)

atom	x	y	z	U_{eq},[a] Å^2
Pd(1)	0.2105(3)	0.0155(7)	0.8004(2)	0.019(5)
Se(11)	0.2710(4)	0.1198(9)	0.7580(4)	0.022(6)
Se(12)	0.2936(4)	0.3032(9)	0.8085(4)	0.035(7)
Se(13)	0.3184(4)	0.2122(10)	0.8908(4)	0.036(8)
Se(14)	0.2393(4)	0.1115(10)	0.8861(4)	0.028(7)
Se(15)	0.1746(4)	−0.0487(10)	0.7104(4)	0.033(7)
Se(16)	0.1313(5)	−0.2370(12)	0.7184(5)	0.058(10)
Se(17)	0.0933(5)	−0.1758(12)	0.7817(5)	0.055(8)
Se(18)	0.1655(5)	−0.1088(10)	0.8467(4)	0.041(9)
Pd(2)	0.3928(3)	0.0294(7)	0.5957(2)	0.016(4)
Se(21)	0.4058(4)	0.0373(9)	0.5098(4)	0.027(7)
Se(22)	0.4181(4)	0.2541(10)	0.5000(4)	0.034(7)
Se(23)	0.4852(4)	0.2810(9)	0.5740(4)	0.031(7)
Se(24)	0.4424(4)	0.2151(10)	0.6356(4)	0.029(7)
Se(25)	0.3335(4)	−0.1335(9)	0.5505(4)	0.025(6)
Se(26)	0.3198(4)	−0.2556(9)	0.6198(4)	0.028(6)
Se(27)	0.3066(4)	−0.0905(9)	0.6714(4)	0.026(6)
Se(28)	0.3890(4)	0.0032(10)	0.6850(3)	0.028(7)
Pd(3)	0	0	0	0.029(8)
Se(31)	0.0654(4)	0.1574(10)	0.0381(4)	0.032(8)
Se(32)	0.0840(4)	0.2592(9)	−0.0315(4)	0.026(6)
Se(33)	0.1236(5)	0.1129(11)	−0.0716(4)	0.042(9)
Se(34)	0.0534(5)	−0.0213(12)	−0.1187(5)	0.053(9)
Se(35)	−0.0131(5)	0.0494(10)	−0.0910(4)	0.040(9)

[a] $U_{eq} = {}^1/_3\sum_i\sum_j(U_{ij}a^*_i a^*_j \mathbf{a}_i \cdot \mathbf{a}_j)$.

Table III. Anion Atomic Positions and Equivalent Isotropic Thermal Parameters for α-[PPh$_4$]$_2$[Pt(Se$_4$)$_3$]·DMF (**2**)

atom	x	y	z	U_{eq}, Å^2
Pt	0.190 33(4)	0.264 48(2)	0.773 47(2)	0.0318(2)
Se(1)	0.083 67(10)	0.392 34(6)	0.820 44(6)	0.0402(6)
Se(2)	−0.088 05(11)	0.340 79(7)	0.906 13(6)	0.0477(7)
Se(3)	−0.178 91(10)	0.261 56(7)	0.821 72(6)	0.0481(6)
Se(4)	0.007 08(10)	0.169 96(6)	0.810 12(6)	0.0415(6)
Se(5)	0.378 11(10)	0.355 44(6)	0.735 34(6)	0.0400(6)
Se(6)	0.465 78(11)	0.370 15(6)	0.854 64(6)	0.0478(7)
Se(7)	0.486 58(10)	0.230 74(6)	0.899 33(6)	0.0452(6)
Se(8)	0.259 74(10)	0.203 82(6)	0.904 36(5)	0.0395(6)
Se(9)	0.094 48(10)	0.323 99(6)	0.648 36(6)	0.0410(6)
Se(10)	0.237 04(11)	0.264 92(7)	0.555 25(6)	0.0463(7)
Se(11)	0.224 01(11)	0.128 28(6)	0.608 76(6)	0.0468(7)
Se(12)	0.312 68(11)	0.139 67(6)	0.728 89(6)	0.0435(7)

Crystallographic Studies

Intensity data were collected from single crystals with the use of Picker and Enraf-Nonius CAD4 diffractometers. Crystals of **1** were of marginal quality. The data for **1**–**4** were processed by methods standard in the laboratory[34] and then corrected for absorption. The positions of the heavy atoms of all four structures were located with the SHEL86 direct methods program;[35] the structures were refined with the SHELXS-92 least-squares program,[36] and the results were analyzed with the SHELXTL PC[37] graphics programs. In **1** only the heavy atoms were refined anisotropically; the light atoms were refined isotropically. All non-hydrogen atoms in **2**[38] (except those of the DMF of solvation), **3**, and **4** were refined anisotropically. Prior to the final refinement, hydrogen atoms were included at calculated positions. Some crystallographic details are listed in Table I. The final positional parameters and equivalent isotropic thermal parameters of all non-hydrogen atoms are given in Tables II–V. Additional crystallographic details are given in supplementary Tables SI–SXIII.[39]

Results and Discussion

Synthesis. Our recent discoveries of the NEt$_4^+$ salts of the Ni^{IV} cubanes[27,28] [Ni$_4$Se$_4$(Se$_3$)$_5$(Se$_4$)]$^{4-}$ and [Ni$_4$Te$_4$(Te$_2$)$_2$(Te$_3$)$_4$]$^{4-}$

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(33) The α and β notation is not strictly correct, because **2** crystallizes with DMF in the unit cell and **3** does not, but the use of α and β helps to differentiate the two compounds.

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(38) The refinement of **2** is based on a new data set collected from a crystal that is better than the one used previously in ref 25.

(39) Supplementary material.

Table IV. Anion Atomic Positions and Equivalent Isotropic Thermal Parameters for β-$[PPh_4]_2[Pt(Se_4)_3]$ (**3**)

atom	*x*	*y*	*z*	U_{eq}, Å^2
Pt	0.317 36(3)	0.312 61(4)	0.620 89(1)	0.0189(2)
Se(1)	0.417 66(8)	0.306 78(11)	0.565 26(3)	0.0265(6)
Se(2)	0.498 19(10)	0.127 10(13)	0.576 17(4)	0.0399(8)
Se(3)	0.577 83(9)	0.160 20(13)	0.639 72(4)	0.0395(6)
Se(4)	0.430 42(9)	0.191 41(12)	0.669 18(3)	0.0309(6)
Se(5)	0.196 08(10)	0.446 84(11)	0.581 37(4)	0.0340(7)
Se(6)	0.112 72(9)	0.330 86(12)	0.530 97(3)	0.0318(6)
Se(7)	0.068 55(9)	0.177 04(13)	0.568 85(4)	0.0349(6)
Se(8)	0.234 67(8)	0.124 01(10)	0.599 56(3)	0.0252(6)
Se(9)	0.410 41(9)	0.498 21(11)	0.638 50(4)	0.0311(6)
Se(10)	0.388 48(10)	0.530 25(12)	0.703 89(4)	0.0365(7)
Se(11)	0.214 46(10)	0.491 01(13)	0.698 16(4)	0.0395(7)
Se(12)	0.213 85(9)	0.300 67(12)	0.675 79(3)	0.0319(6)

Table V. Anion Atomic Positions and Equivalent Isotropic Thermal Parameters for $[PPh_4]_2[Pt(Se_4)_2]$ (**4**)

atom	*x*	*y*	*z*	U_{eq}, Å^2
Pt	0.645 40(2)	0.171 54(2)	0.230 92(2)	0.01381(9)
Se(1)	0.799 24(7)	0.241 63(6)	0.140 07(5)	0.0201(3)
Se(2)	0.981 69(7)	0.230 73(6)	0.230 79(6)	0.0241(3)
Se(3)	0.970 15(7)	0.083 70(6)	0.270 80(6)	0.0230(3)
Se(4)	0.774 45(7)	0.083 99(6)	0.334 23(5)	0.0212(3)
Se(5)	0.516 61(7)	0.280 73(5)	0.153 99(5)	0.0189(3)
Se(6)	0.317 34(7)	0.221 04(6)	0.146 69(6)	0.0228(3)
Se(7)	0.316 62(6)	0.169 97(7)	0.300 68(5)	0.0263(3)
Se(8)	0.489 93(7)	0.079 51(6)	0.294 42(5)	0.0198(3)

Table VI. Anion Bond Distances (Å) and Angles (deg) for $[NEt_4]_5[2Pd(Se_4)_2 \cdot {}^1/_2Pd(Se_5)_2]$ (**1**)

Pd(1)–Se(11)	2.489(12)	Pd(2)–Se(21)	2.408(11)
Pd(1)–Se(14)	2.410(11)	Pd(2)–Se(24)	2.437(12)
Pd(1)–Se(15)	2.406(12)	Pd(2)–Se(25)	2.419(11)
Pd(1)–Se(18)	2.358(13)	Pd(2)–Se(28)	2.422(11)
Se(11)–Se(12)	2.333(14)	Se(21)–Se(22)	2.334(14)
Se(13)–Se(14)	2.353(15)	Se(23)–Se(24)	2.362(14)
Se(15)–Se(16)	2.343(16)	Se(25)–Se(26)	2.362(14)
Se(17)–Se(18)	2.314(17)	Se(27)–Se(28)	2.364(14)
Se(12)–Se(13)	2.307(15)	Se(22)–Se(23)	2.278(15)
Se(16)–Se(17)	2.299(17)	Se(26)–Se(27)	2.306(14)

Se(11)–Pd(1)–Se(14)	99.6(4)	Se(21)–Pd(2)–Se(24)	100.1(4)
Se(15)–Pd(1)–Se(18)	104.0(5)	Se(25)–Pd(2)–Se(28)	101.4(4)
Se(11)–Pd(1)–Se(15)	78.7(4)	Se(21)–Pd(2)–Se(25)	79.0(4)
Se(14)–Pd(1)–Se(18)	79.3(4)	Se(24)–Pd(2)–Se(28)	80.6(4)
Se(11)–Pd(1)–Se(18)	169.7(5)	Se(21)–Pd(2)–Se(28)	172.8(5)
Se(14)–Pd(1)–Se(15)	170.8(5)	Se(24)–Pd(2)–Se(25)	171.7(5)
Pd(1)–Se(11)–Se(12)	101.7(5)	Pd(2)–Se(21)–Se(22)	101.7(5)
Pd(1)–Se(14)–Se(13)	106.4(5)	Pd(2)–Se(24)–Se(23)	104.5(5)
Pd(1)–Se(15)–Se(16)	102.5(5)	Pd(2)–Se(25)–Se(26)	103.2(5)
Pd(1)–Se(18)–Se(17)	103.2(5)	Pd(2)–Se(28)–Se(27)	101.5(5)
Se(11)–Se(12)–Se(13)	99.1(5)	Se(21)–Se(22)–Se(23)	97.4(5)
Se(12)–Se(13)–Se(14)	97.2(5)	Se(22)–Se(23)–Se(24)	97.9(5)
Se(15)–Se(16)–Se(17)	99.6(6)	Se(25)–Se(26)–Se(27)	97.9(5)
Se(16)–Se(17)–Se(18)	100.1(6)	Se(26)–Se(27)–Se(28)	96.2(5)

Pd(3)–Se(31)	2.422(10)	Se(34)–Se(35)	2.252(17)
Pd(3)–Se(35)	2.399(10)	Se(32)–Se(33)	2.303(14)
Se(31)–Se(32)	2.317(13)	Se(33)–Se(34)	2.408(17)

Se(31)–Pd(3)–Se(35)	98.8(3)	Se(31)–Se(32)–Se(33)	107.1(5)
Se(31)–Pd(3)–Se(35a)	81.2(3)	Se(33)–Se(34)–Se(35)	102.5(6)
Pd(3)–Se(31)–Se(32)	106.3(4)	Se(32)–Se(33)–Se(34)	103.5(6)
Pd(3)–Se(35)–Se(34)	110.9(6)		

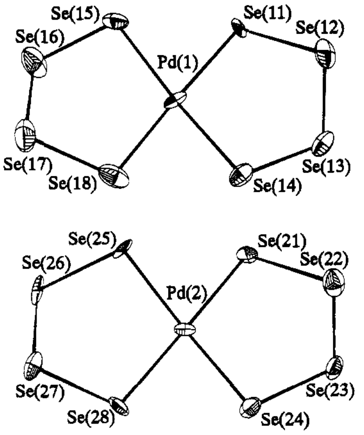

Figure 1. The two independent $[Pd(Se_4)_2]^{2-}$ anions in $[NEt_4]_5[2Pd(Se_4)_2 \cdot {}^1/_2Pd(Se_5)_2]$ (**1**). In this figure and in Figures 2–5 the 50% probability ellipsoids are shown.

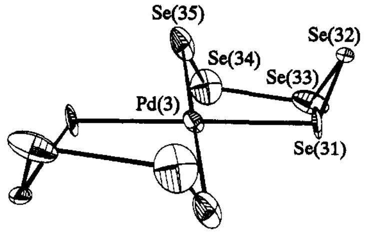

Figure 2. The $[Pd(Se_5)_2]^{2-}$ ion in $[NEt_4]_5[2Pd(Se_4)_2 \cdot {}^1/_2Pd(Se_5)_2]$ (**1**). The anion has a crystallographically imposed center of symmetry.

caused us to search for similar salts of Pd and Pt. Attempts to isolate a Pd^{IV} cubane have been unsuccessful, but reaction of $Pd(xan)_2$ with a large excess of polyselenide (Pd:Se ratio 1:15) in the presence of NEt_4Cl affords $[NEt_4]_5[2Pd(Se_4)_2 \cdot {}^1/_2Pd(Se_5)_2]$ (**1**), which contains the previously unknown $[Pd(Se_5)_2]^{2-}$ anion. Perhaps $[Pd(Se_4)_2]^{2-}$ and $[Pd(Se_5)_2]^{2-}$ exist in equilibrium in solution via a $[Pd(Se_4)(Se_5)]^{2-}$ intermediate, but ^{77}Se NMR spectroscopy has provided no evidence for this intermediate.

From the reaction of $Pt(xan)_2$ with polyselenide species in DMF only the monomeric anions $[Pt(Se_4)_2]^{2-}$ and $[Pt(Se_4)_3]^{2-}$ have been isolated. (The PPh_4^+ salts of these anions are described here, but similar products form in the presence of NEt_4^+.) The reaction of $Pt(xan)_2$ with excess polyselenide species yields exclusively $[Pt(Se_4)_3]^{2-}$. The crystals of $[PPh_4]_2[Pt(Se_4)_3]$ obtained from the initial filtrate are the α form (ΔλλΔ and Λδδλ racemates). If one decants the solution of the crystals and further dilutes it with ether, then one obtains a mixture of the α and β forms (Δλδδ and Λδλλ racemates). Crystals of the two forms are easily differentiated and may be separated by hand: the α form has an equant habit while the β form has a needle habit. Repeated examination of the first crop of crystals from several reactions indicates that the β form was not present; the β form apparently crystallizes only from the dilute solutions.

Attempts to prepare pure $[Pt(Se_4)_2]^{2-}$ by limiting the amount of polyselenide solution were unsuccessful. ^{77}Se NMR spectroscopic studies of reaction filtrates with a Pt:Se ratio ≤1:6 indicate that the solution contains a mixture of $[Pt(Se_4)_2]^{2-}$ and $[Pt(Se_4)_3]^{2-}$. The reaction of $PtCl_2$ with 3 equiv of Li_2Se_5 reportedly yields $[Pt(Se_4)_2]^{2-}$,[15] but we were unable to duplicate this synthesis. Our experience with Pt and polyselenide species suggests that when excess polyselenide is present, Pt^{II} is oxidized to Pt^{IV}. An alternative route to $[Pt(Se_4)_2]^{2-}$ by the reduction of $[Pt(Se_4)_3]^{2-}$ with $LiBEt_3H$ has been developed.[13] In this reaction Pt^{IV} is reduced to Pt^{II} with concomitant loss of one Se_4^{2-} ligand to afford $[Pt(Se_4)_2]^{2-}$:

$$[Pt^{IV}(Se_4)_3]^{2-} + 2e^- \rightarrow [Pt^{II}(Se_4)_2]^{2-} + Se_4^{2-}$$

Structure of $[NEt_4]_5[2Pd(Se_4)_2 \cdot {}^1/_2Pd(Se_5)_2]$ (1). Owing to the poor quality of the crystals, the metrical details for $[NEt_4]_5[2Pd(Se_4)_2 \cdot {}^1/_2Pd(Se_5)_2]$ in Table VI have large uncertainties. The asymmetric unit contains five independent NEt_4^+ cations, two independent $[Pd(Se_4)_2]^{2-}$ anions (Figure 1), and one-half of a $[Pd(Se_5)_2]^{2-}$ anion (Figure 2). The C–N–C angles of the cations range from 91(6) to 121(8)°, and the N–C–C angles range from 106(9) to 126(10)°. The mean N–C bond length is 1.51(8) Å, and the mean C–C bond length is 1.48(12) Å. Further details on the cations are available.[39]

Each $[Pd(Se_4)_2]^{2-}$ anion has the expected two bidentate Se_4^{2-} chains attached to a Pd center in nearly a square-planar coordination (Figure 1). The Pd(1)–Se distances (Table VI)

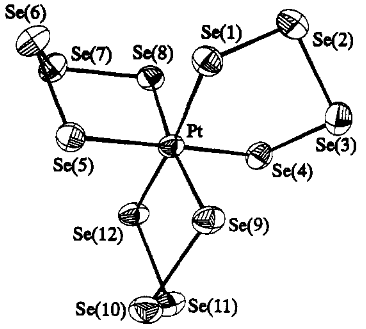

Figure 3. The α-$[Pt(Se_4)_3]^{2-}$ ion in $[PPh_4]_2[Pt(Se_4)_3]\cdot$DMF (**2**). The $\Delta\lambda\lambda\delta$ conformer is shown.

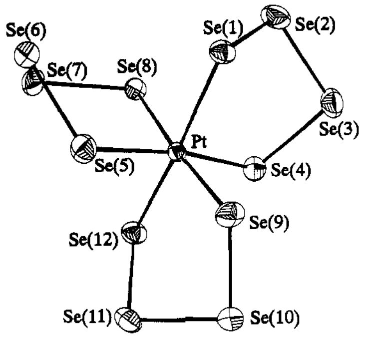

Figure 4. The β-$[Pt(Se_4)_3]^{2-}$ ion in $[PPh_4]_2[Pt(Se_4)_3]$ (**3**). The $\Delta\lambda\delta\delta$ conformer is shown.

vary from 2.358(13) to 2.489(12) Å, and the Pd(2)–Se distances vary from 2.408(11) to 2.437(12) Å. The average deviations of Se_{mb} atoms (mb denotes "metal-bound") from the least-squares planes through the $Pd(Se_{mb})_4$ units are 0.20 and 0.16 Å for Pd(1) and Pd(2), respectively. In the PPh_4^+ salt of $[Pd(Se_4)_2]^{2-}$, the mean Pd–Se distance is 2.421(19) Å and the average deviation of Se_{mb} from the least-squares plane is 0.27 Å.[15] The Se–Se distances of the present $PdSe_4$ five-membered rings (Table VI) exhibit the characteristic Se_{mb}–Se_r and Se_r–Se_r long–short bond length alternation (r denotes "ring") found previously in the d^8 $[M(Se_4)_2]^{2-}$ system (M = Ni, Pd, Pt).[13] The bond alternation is attributed to donation of electron density from the Se_{mb} atom to the metal center with concomitant decrease in the Se_{mb}–Se_r bond strength[13]. The Pd(2)Se(21–24) five-membered ring has a distorted envelope configuration while the three other $PdSe_4$ five-membered rings adopt the half-chair configuration of cyclopentane. The MSe_4 rings in the PPh_4^+ salts of the $[M(Se_4)_2]^{2-}$ (M = Ni,[12] Pd,[15] Pt) anions exhibit the half-chair conformation. Torsion angles for the MSe_4 rings in the present Pd complex and in the PPh_4^+ salts of $[M(Se_4)_2]^{2-}$ (M = Ni, Pd, Pt) are listed in Table IX.

The $[Pd(Se_5)_2]^{2-}$ anion consists of a square-planar Pd center chelated by two Se_5^{2-} chains that are related by a crystallographically imposed center of symmetry through the Pd atom (Figure 2). $[Pd(Se_5)_2]^{2-}$ is the first square-planar transition-metal anion with two Q_5 ligands to be characterized crystallographically. Recently, the analogous square-planar main-group anions $[Se(Se_5)_2]^{2-}$,[40–42] $[Te(Se_5)_2]^{2-}$,[43] and $[Te(S_5)_2]^{2-}$ [42] were structurally characterized. The MQ_5 six-membered rings in these main-group anions and all other mononuclear MQ_5 species[5,7] (including the PdS_5 six-membered ring in $[Pd(S_3N)(S_5)]^{2-}$ [44]) adopt the chair conformation of cyclohexane, but the $PdSe_5$ six-membered ring in the present complex adopts the boat conformation (Figure 2). Table X lists the torsion angles in $[Pd(Se_5)_2]^{2-}$ and other MQ_5 systems. The Pd–Se_{mb} distances of 2.422(10) and 2.399(10) Å in the $[Pd(Se_5)_2]^{2-}$ anion are similar to the Pd–Se distances in the $[Pd(Se_4)_2]^{2-}$ anions. The Se–Se bond lengths vary around the $PdSe_5$ ring with no discernible pattern.

Structures of α-$[PPh_4]_2[Pt(Se_4)_3]\cdot$DMF (2) and β-$[PPh_4]_2[Pt(Se_4)_3]$ (3). We have isolated two different diastereomers (and their racemates) of $[Pt(Se_4)_3]^{2-}$. The α form contains the $\Delta\lambda\lambda\delta$ (Figure 3) and $\Lambda\delta\delta\lambda$ racemates, and the β form contains the $\Delta\lambda\delta\delta$ (Figure 4) and $\Lambda\delta\lambda\lambda$ racemates. β-$[PPh_4]_2[Pt(Se_4)_3]$ is isostructural with $[PPh_4]_2[Sn(Se_4)_3]$,[45,46] which also contains the $\Delta\lambda\delta\delta$ and $\Lambda\delta\lambda\lambda$ racemates.[47] In Figure 3, which depicts the α-$[Pt(Se_4)_3]^{2-}$ ion, the rings containing atoms Se(5–8) and atoms Se(9–12) have the λ configuration and the ring containing atoms Se(1–4) has the δ configuration. In Figure 4, which shows the β-$[Pt(Se_4)_3]^{2-}$ ion, the ring containing atoms Se(5–8) has the λ configuration and the rings containing atoms Se(1–4) and atoms Se(9–12) have the δ configuration. In the $[M(en)_3]^{n+}$ systems (en = ethylenediamine), thermodynamic considerations[48] and NMR spectroscopy[49] indicate the relative stabilities of the different conformers in solution to be $\Delta\lambda\lambda\delta > \Delta\lambda\lambda\lambda \approx \Delta\lambda\delta\delta > \Delta\delta\delta\delta$. While the large excess of α-$[PPh_4]_2[Pt(Se_4)_3]$ compared with β-$[PPh_4]_2[Pt(Se_4)_3]$ that occurs during synthesis is at least consistent with this order, what influence the DMF of solvation has on the conformation of the anion in the α salt is unknown. A comparison of inter-ring interactions in each of the $[Pt(Se_4)_3]^{2-}$ anions reveals no substantive differences out to 3.5 Å. Intracomplex interactions are apparently not responsible for the differences in conformational stabilities, as they are believed to be in the $[M(en)_3]^{n+}$ systems. But note that in the analogous tin system, $[Sn(Se_4)_3]^{2-}$, only the $\Delta\lambda\delta\delta$ conformer occurs[45,46] and in α- and β-$[NH_4]_2[Pt(S_5)_3]$ and α-$K_2[Pt(S_5)_3]$[21] the $[Pt(S_5)_3]^{2-}$ ion has the $\Delta\lambda\lambda\lambda$ conformation. Obviously, numerous factors affect which isomer of $[M(Q_n)_3]^{2-}$ (n = 4, 5) will crystallize from a given system.

The average intra-ring distances (Table VII) in the two different conformers of $[Pt(Se_4)_3]^{2-}$ are almost identical. Thus Pt–Se_{mb} = 2.488(6) Å (α), 2.488(5) Å (β), Se_{mb}–Se_r = 2.339(5) Å (α), 2.339(15) Å (β), and Se_r–Se_r = 2.325(4) Å (α), 2.318(5) Å (β). The Se_4 rings attached to the d^6 Pt center follow the trend in Se–Se bond alternation found in the d^2 and d^8 systems.[13,50] On the other hand, the Se_4 rings in the $[Sn(Se_4)_3]^{2-}$ anion, a d^{10} system, do not show the trends seen in the d^{10} $[M(Se_4)_2]^{2-}$ anions (M = Zn, Cd, Hg).[13] But the Sn atom in the $[Sn(Se_4)_3]^{2-}$ ion has bonding contributions from its 5d orbitals and this may account for this difference. The inter-ring and intra-ring angles are similar in both $[Pt(Se_4)_3]^{2-}$ isomers and in $[Sn(Se_4)_3]^{2-}$ and the intra-ring angles do not vary significantly between the λ and δ conformers of the rings. Except for the MSe(1–4) (M = β-Pt, Sn) rings, which adopt the envelope conformation, the five-membered rings adopt the half-chair conformation. Torsion angles are listed in Table IX.

Both salts have unremarkable PPh_4^+ counterions that do not interact with the $PtSe_4$ rings. The P–C and C–C distances differ little between the complexes with mean distances of 1.794(11)

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(47) The Δ/Λ and δ/λ notation is defined as follows: With the metal center being viewed down a pseudo-3-fold axis (see Figure 3), the Se_4 chains are positioned front-to-back clockwise in the Δ configuration and counterclockwise in the Λ configuration. Given the Δ configuration (as in Figure 3), the Se_r atoms are perpendicular to the pseudo-3-fold axis in the δ conformation and parallel in the λ conformation. In the Λ configuration the δ/λ qualifiers are reversed. See ref 48 for further details on the notation.

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Table VII. Anion Bond Distances (Å) and Angles (deg) for α-$[PPh_4]_2[Pt(Se_4)_3]\cdot DMF$ (**2**) and β-$[PPh_4]_2[Pt(Se_4)_3]$ (**3**)

	2	**3**
Pt–Se(1)	2.491(1)	2.482(1)
Pt–Se(4)	2.488(1)	2.490(2)
Pt–Se(5)	2.491(1)	2.480(2)
Pt–Se(8)	2.478(1)	2.491(2)
Pt–Se(9)	2.484(1)	2.493(2)
Pt–Se(12)	2.494(1)	2.491(1)
Se(1)–Se(2)	2.336(2)	2.329(2)
Se(3)–Se(4)	2.335(2)	2.346(2)
Se(5)–Se(6)	2.334(2)	2.332(2)
Se(7)–Se(8)	2.348(2)	2.365(2)
Se(9)–Se(10)	2.341(2)	2.340(2)
Se(11)–Se(12)	2.340(2)	2.322(2)
Se(2)–Se(3)	2.328(2)	2.315(2)
Se(6)–Se(7)	2.321(2)	2.323(2)
Se(10)–Se(11)	2.325(2)	2.315(2)
	Intrachelate	
Se(1)–Pt–Se(4)	99.50(4)	99.58(5)
Se(5)–Pt–Se(8)	99.12(4)	99.38(5)
Se(9)–Pt–Se(12)	99.21(4)	99.60(5)
Pt–Se(1)–Se(2)	102.01(5)	100.42(6)
Pt–Se(4)–Se(3)	102.37(5)	104.40(6)
Pt–Se(5)–Se(6)	103.40(5)	104.26(6)
Pt–Se(8)–Se(7)	102.73(5)	104.02(6)
Pt–Se(9)–Se(10)	102.50(5)	104.08(6)
Pt–Se(12)–Se(11)	103.80(5)	102.94(6)
Se(1)–Se(2)–Se(3)	97.52(5)	97.96(7)
Se(2)–Se(3)–Se(4)	96.26(6)	98.34(7)
Se(5)–Se(6)–Se(7)	96.55(5)	98.51(7)
Se(6)–Se(7)–Se(8)	97.99(5)	98.99(6)
Se(9)–Se(10)–Se(11)	97.55(5)	98.50(7)
Se(10)–Se(11)–Se(12)	97.84(5)	99.64(7)
	Interchelate	
Se(1)–Pt–Se(5)	82.28(4)	88.07(5)
Se(1)–Pt–Se(8)	94.45(4)	90.46(5)
Se(1)–Pt–Se(9)	82.81(4)	84.99(5)
Se(1)–Pt–Se(12)	175.92(4)	175.17(5)
Se(4)–Pt–Se(5)	178.22(3)	171.53(4)
Se(4)–Pt–Se(8)	80.70(4)	84.32(5)
Se(4)–Pt–Se(9)	93.96(4)	95.37(5)
Se(4)–Pt–Se(12)	83.94(4)	78.61(5)
Se(5)–Pt–Se(9)	86.34(4)	81.57(5)
Se(5)–Pt–Se(12)	94.28(4)	94.05(5)
Se(8)–Pt–Se(9)	173.55(4)	175.33(4)
Se(8)–Pt–Se(12)	83.89(4)	84.92(5)

Table VIII. Anion Bond Distances (Å) and Angles (deg) for $[PPh_4]_2[Pt(Se_4)_2]$ (4)

Pt–Se(1)	2.412(1)	Se(1)–Se(2)	2.347(1)
Pt–Se(4)	2.409(1)	Se(3)–Se(4)	2.358(1)
Pt–Se(5)	2.424(1)	Se(5)–Se(6)	2.369(1)
Pt–Se(8)	2.412(1)	Se(7)–Se(8)	2.357(1)
		Se(2)–Se(3)	2.326(2)
		Se(6)–Se(7)	2.320(1)
Se(1)–Pt–Se(4)	99.50(3)	Pt–Se(4)–Se(3)	107.03(4)
Se(5)–Pt–Se(8)	99.34(3)	Pt–Se(5)–Se(6)	106.03(4)
Se(1)–Pt–Se(5)	81.99(3)	Pt–Se(8)–Se(7)	104.66(4)
Se(4)–Pt–Se(8)	81.73(3)	Se(1)–Se(2)–Se(3)	98.61(5)
Se(1)–Pt–Se(8)	167.79(3)	Se(2)–Se(3)–Se(4)	98.59(5)
Se(4)–Pt–Se(5)	168.14(3)	Se(5)–Se(6)–Se(7)	97.06(4)
Pt–Se(1)–Se(2)	105.98(4)	Se(6)–Se(7)–Se(8)	97.64(4)

Table IX. Torsion Angles[a] (deg) in Selected MSe_4 Rings

complex	MSe_4 ring	M–Se(a)–Se(b)–Se(c)–Se(d)–M				
1	Pd(1)Se(11–14)	−23.4	52.0	−58.8	44.0	−12.4
	Pd(1)Se(15–18)	−15.0	42.9	−55.2	45.6	−18.3
	Pd(2)Se(21–24)	−27.9	55.8	−59.7	42.0	−8.1
	Pd(2)Se(25–28)	−12.3	46.0	−61.2	53.8	−24.8
2	PtSe(1–4)	18.2	−50.8	64.3	−52.0	20.5
	PtSe(5–8)	−19.9	50.8	−62.5	50.1	−18.0
	PtSe(9–12)	−22.3	52.2	−61.7	47.2	−15.0
3	PtSe(1–4)	29.0	−56.3	61.2	−41.4	7.5
	PtSe(5–8)	−20.4	49.3	−58.4	45.5	−15.1
	PtSe(9–12)	15.8	−45.8	59.3	−49.1	19.8
$[Sn(Se_4)_3]^{2-}$ [b]	SnSe(1–4)	31.0	58.0	62.8	−37.5	3.9
	SnSe(5–8)	−21.7	50.8	−63.5	45.0	−13.5
	SnSe(9–12)	17.4	−47.2	62.9	−48.4	17.9
$[Ni(Se_4)_2]^{2-}$ [c]	NiSe(1–4)	−20.9	48.2	−53.3	43.7	−14.0
	NiSe(5–8)	−14.4	41.9	−49.8	44.9	−18.9
$[Pd(Se_4)_2]^{2-}$ [d]	PdSe(1–4)	−20.2	46.9	−53.9	42.1	−13.5
	PdSe(5–8)	−13.9	44.6	−57.7	50.1	−21.8
4	PtSe(1–4)	−20.2	47.1	−53.3	42.7	−13.8
	PtSe(5–8)	−14.5	45.5	−57.2	50.6	−21.5

[a] The torsion angle *W*(IJKL) is defined as the angle between the vector JI and the vector KL when viewed down JK. The sign of *W* is positive if JI is to be rotated clockwise into KL and negative if it is to be rotated counterclockwise. [b] Reference 45. [c] Reference 12. [d] Reference 15.

Table X. Torsion Angles (deg) in Selected MSe_5 and MS_5 Rings

complex	MSe_5 ring	M–Se(a)–Se(b)–Se(c)–Se(d)–Se(e)–M					
1	Pd(3)Se-(31–35)	−3.8	−67.1	74.8	−7.1	−68.0	74.7
$[Se(Se_5)_2]^{2-}$ [a]	SeSe(1–5)	−50.1	69.3	−83.0	81.3	−64.4	46.9
$Cp_2Ti(Se_5)$[b]	TiSe(1–5)	−67.1	75.9	−77.3	76.6	−73.0	66.0
$[Pd(S_3N)(S_5)]^{-}$ [c]	PdS(1–5)	−59.2	75.0	−78.4	76.8	−73.9	59.8

[a] Reference 40. [b] Reference 54. [c] Reference 44.

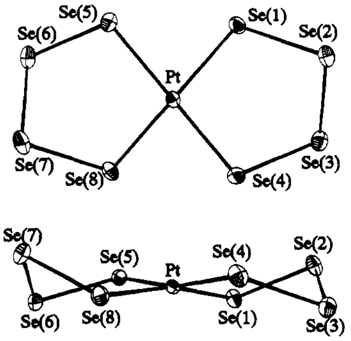

Figure 5. The $[Pt(Se_4)_2]^{2-}$ ion in $[PPh_4]_2[Pt(Se_4)_2]$ (4). Views perpendicular and parallel to the square plane are shown.

Å (α), 1.796(12) Å (β) and 1.385(16) Å (α), 1.381(17) Å (β), respectively. The angles are as expected with C–P–C ranges of 107.1(4)–111.4(1)° (α) and 106.3(5)–111.2(5)° (β), P–C–C ranges of 116.9(7)–122.2(7)° (α) and 118.0(8)–122.2(8)° (β), and C–C–C ranges of 118.2(9)–122.3(8)° (α) and 117.5(10)–122.2(10)° (β). Further details are available.[39]

Structure of $[PPh_4]_2[Pt(Se_4)_2]$ (4). The compounds $[PPh_4]_2[M(Se_4)_2]$ (M = Ni,[12] Pd,[15] Pt) are isostructural; in these, the $[M(Se_4)_2]^{2-}$ ion has a slightly distorted square-planar arrangement of bidentate Se_4^{2-} chains about M (Figure 5). In the present anion, the mean distances are as follows: Pt–Se_{mb}, 2.414(6) Å; Se_{mb}–Se_T, 2.358(9) Å; Se_T–Se_T, 2.323(4) Å. The Se–Se bond lengths follow the alternation characteristic of the d^8 selenometalates. Both $PtSe_4$ five-membered rings adopt the half-chair conformation (see Table IX for the ring torsion angles in the $[PPh_4]_2[M(Se_4)_2]$ (M = Ni, Pd, Pt) complexes). The average deviations of the Se_{mb} atoms from the least-squares planes are 0.33, 0.27, and 0.25 Å for Ni, Pd, and Pt, respectively. This decrease could be a manifestation of the increasing stability of the square-planar configuration on going from Ni to Pt.

The PPh_4^+ counterions in 4 have their expected geometry. The P–C and C–C bond lengths average 1.791(7) and 1.386(14) Å, respectively. The C–P–C, P–C–C, and C–C–C angles range from 104.8(3) to 113.1(3), 117.9(6) to 122.8(6), and 118.1(7) to 122.6(8)°, respectively. Further details are available.[39]

^{77}Se NMR Spectroscopy of $[NEt_4]_5[2Pd(Se_4)_2\cdot{}^1/_2Pd(Se_5)_2]$ (1). The $[Pd(Se_4)_2]^{2-}$ ion is well-known, and its stability in solution on the NMR time scale has been confirmed previously.[13] The Se_4^{2-} chains are fluxional in solution and exhibit two ^{77}Se peaks, one resonance from the four Se_{mb} centers at 893 ppm and one resonance from the four Se_T centers at 758 ppm, the assignment being based on that made for the $[Pt(Se_4)_2]^{2-}$ anion (see below). The $[Pd(Se_5)_2]^{2-}$ anion exhibits three resonances, so the $PdSe_5$ rings must be fluxional at room temperature. From the assignments in the $[Pt(Se_4)_2]^{2-}$ anion[13] and in $(\eta^5\text{-}C_5H_4\text{-}^iPr)_2Ti(Se_5)$,[51] the resonances at 509, 647, and 875 ppm are assigned to the Se bound only to Se, the Se bound to Se and Se_{mb}, and to Se_{mb}, respectively.

^{77}Se and ^{195}Pt NMR Spectroscopy of $[Pt(Se_4)_3]^{2-}$. At room temperature the $Se_4{}^{2-}$ chains in the $[Pt(Se_4)_3]^{2-}$ anion are fluxional, as two lines at 680 and 790 ppm are observed in the ^{77}Se NMR spectrum; one line at −4217 ppm is observed in the ^{195}Pt NMR spectrum. No coupling between the Pt and Se nuclei is visible, so an unequivocal assignment of the resonance of Se_{mb} is impossible. Failure to observe M–Se coupling is normal. Thus no coupling is observed in the closely related $[Sn(Se_4)_3]^{2-}$ species[46] or in numerous tungsten species;[31,50] coupling is observed in the spectrum of $[Pt(Se_4)_2]^{2-}$ (see below). Since the Se–Se bonds in both the α and β forms of $[PPh_4]_2[Pt(Se_4)_3]$ have the Se–Se bond alternation seen in those d^2 and d^8 selenometalates with $Se_4{}^{2-}$ chelates,[13,50] similar assignments should apply and hence the resonances at 680 and 790 ppm probably arise from the Se_r and Se_{mb} atoms, respectively.[52]

In the solid state the $[Pt(Se_4)_3]^{2-}$ anion crystallizes preferentially as the $\Delta\lambda\lambda\delta$ and $\Lambda\delta\delta\lambda$ racemates (the α form) and under slightly different conditions as the $\Delta\lambda\delta\delta$ and $\Lambda\delta\lambda\lambda$ racemates (the β form). Studies[50,53] directed at freezing out different conformations of MQ_4 five-membered rings have previously failed because, unlike MQ_5 six-membered rings, the five-membered rings do not undergo a true inversion to change conformation, but only a pseudorotation. The energy barrier is small, and even at −60 °C the five-membered rings remain fluxional.[53] However, the rings in the $[Pt(Se_4)_3]^{2-}$ anion could be more constrained than those in the $[M(Se_4)_2]^{2-}$ anions (M = Ni, Pd, Pt, Zn, Cd, Hg), owing to interactions between the rings in the comparatively cramped octahedral configuration. Therefore a study of this system at low temperature was undertaken. The results were surprising, although observation of the different isomers of $[Pt(Se_4)_3]^{2-}$ was unsuccessful. As seen in Figure 6, when a solution of $[PPh_4]_2[Pt(Se_4)_3]$ in a 50:50 DMF:CH_2Cl_2 solution is cooled from 20 to 10 °C, the ^{77}Se spectrum changes dramatically from a two-line spectrum to a seven-line spectrum. As the solution is cooled to −10 °C, the two lines attributable to the $[Pt(Se_4)_3]^{2-}$ anion continue to shrink, and by −30 °C they disappear completely. The new five-line spectrum remains constant down to −60 °C. No matter what distribution of isomers is chosen for $[Pt(Se_4)_3]^{2-}$, a five-line spectrum cannot result except in the highly unlikely event of exact overlap of two lines. Moreover the range of lines from 400 to 900 ppm is greater than we would expect for different isomers of the $[Pt(Se_4)_3]^{2-}$ anion. Finally, independent experiments indicate that by −30 °C essentially all of the $[PPh_4]_2[Pt(Se_4)_3]$ has precipitated. It seems likely that an additional $[Pt_xSe_y]^{z-}$ species is present in solution. Such a species is presumably highly soluble but is present in very low concentration. In this instance the ^{77}Se peaks of the species would be hidden in the noise at room temperature but would become visible as the solution is cooled and the less soluble $[PPh_4]_2[Pt(Se_4)_3]$ precipitates. The ^{195}Pt nucleus has a much greater receptivity than does ^{77}Se, and one additional small peak, which could arise from this hypothetical species, was found at −3783 ppm in the ^{195}Pt spectrum. The ^{77}Se resonances occur in the same range observed for the Ni^{IV} cubane $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$.[27,28] Since $[Pt(Se_4)_3]^{2-}$ and $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ both result from reactions where a M^{II} center is oxidized to a M^{IV} center, some Pt^{IV} cubane may form during the synthesis of the $[Pt(Se_4)_3]^{2-}$ anion. In the Pt–Te system the Pt^{IV} cubane $[Pt_4Te_4(Te_3)_6]^{4-}$ is the dominant species.[29] The hypothetical cubane, $[Pt_4Se_4(Se_3)_4(Se_4)_2]^{4-}$, with the Se_4 chains bridging opposite faces of the cube, should exhibit a five-line ^{77}Se NMR spectrum. Numerous attempts to precipitate such a cubane were unsuccessful.

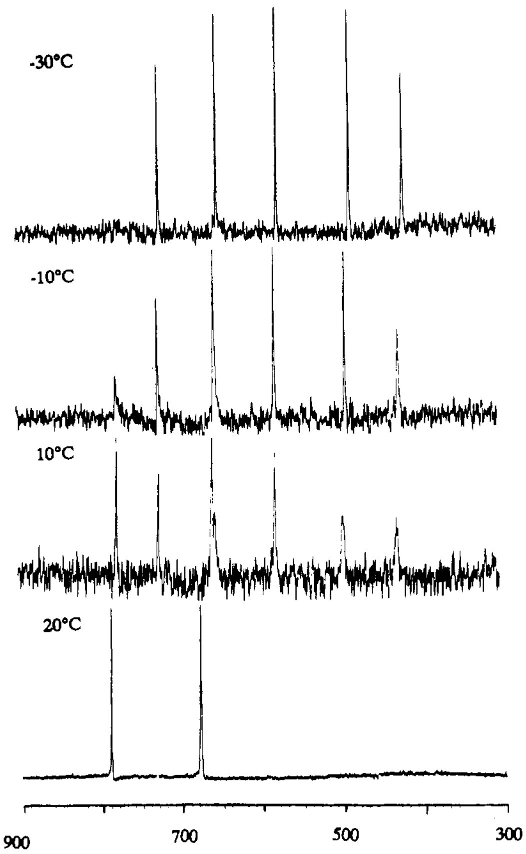

Figure 6. Variable temperature ^{77}Se NMR spectra of $[Pt(Se_4)_3]^{2-}$ in a 50:50 DMF:CH_2Cl_2 solution.

Table XI. ^{77}Se and ^{195}Pt NMR Resonances (ppm)[a]

complex	Se_{mb}	$Se_{r/r1}$[b]	Se_{r2}[c]	Pt
$[Pd(Se_4)_2]^{2-}$	893	758		
$[Pd(Se_5)_2]^{2-}$	875	647	509	
$[Pt(Se_4)_3]^{2-}$	790	680		−4217
$[Pt(Se_4)_2]^{2-}$	747 (384)[d]	642		−4568 (372)[e]

[a] Room-temperature, DMF solvent, $\delta(Me_2Se) = 0$, $\delta(Na_2PtCl_6) = 0$. [b] Se_{r1} refers to the Se atoms in the $PdSe_5$ ring bound to Se_{mb} atoms. [c] Se_{r2} refers to the Se atoms in the $PdSe_5$ ring bound solely to Se_{r1} atoms. [d] $^1J_{Pt-Se}$ satellites (in Hz). [e] $^1J_{Se-Pt}$ satellites (in Hz).

^{77}Se and ^{195}Pt NMR Spectroscopy of $[Pt(Se_4)_2]^{2-}$. The $[Pt(Se_4)_2]^{2-}$ anion has two ^{77}Se NMR resonances at 642 and 747 ppm. The peak at 747 ppm exhibits $^1J_{Se-Pt}$ coupling of 384 Hz and hence is assigned to Se_{mb}. The single resonance at −4568 ppm found in the ^{195}Pt NMR spectrum also exhibits $^1J_{Pt-Se}$ satellites of 372 Hz. Trends in the resonances of Se_{mb} and Se_r as a function of the d-configuration of the metal have been discussed previously.[13] The ^{77}Se and ^{195}Pt chemical shifts of **1**–**4** are summarized in Table XI.

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Supplementary Material Available: Tables of crystallographic details (Table SI), cation and solvent atom parameters (Tables SII–SV), thermal displacement parameters (Tables SVI–SIX), and metrical details on cations and solvent molecules (Tables SX–SXIII) (41 pages). Ordering information is given on any current masthead page.

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(52) The previous report[25] of $^{195}Pt-^{77}Se$ coupling in $[Pt(Se_4)_3]^{2-}$ was incorrect; the 680 and 790 ppm peaks cannot be assigned unambiguously.

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