Anion and Solvent Effects upon the Structures of Platinum(II) Complexes with Thiacrown Ligands: The Crystal Structures of $[Pt(9S3)_2](PF_6)_2 \cdot 2\ CH_3NO_2$, $[Pt(9S3)_2](BF_4)_2 \cdot 2\ CH_3NO_2$, $[Pt(9S3)_2](OTf)_2 \cdot 2\ CH_3NO_2$, and $[Pt(18S6)](BF_4)_2$

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The synthesis and crystal structures of four mononuclear Pt^{II} homoleptic complexes with two thiacrown ligands are presented. The binding mode for both macrocycles to the platinum center contrasts with previous structural reports involving identical complex cations but differing anions or crystallization solvents. All three bis(1,4,7-trithiacyclononane(9S3))platinum(II) complexes (with tetrafluoroborate, hexafluorophosphate, and triflate as counterions) are centrosymmetric, with *endodentate* binding of the trithioether resulting in $[S_4 + S_2]$ coordination. The Pt^{II} complex of 1,4,7,10,13,16-hexathiacyclooctadecane(18S6) shows an elongated square pyramidal structure with one *exodentate* sulfur in a $[S_4 + S_1]$ mode. Our work illustrates how changes of counterion and solvent dramatically affect the crystal structures for such complexes, suggesting that packing forces are more important than ligand conformation in determining solid-state structures. In addition, the full spectroscopic and electrochemical properties of the complex $[Pt(18S6)](BF_4)_2$ are reported. The electronic spectrum shows a d–d transition near 430 nm, and an irreversible Pt^{II}/Pt^{III} couple occurs at +564 mV vs. Fc/Fc^+ in cyclic voltammetry. Both these data are consistent with other hexakis(thioether) Pt^{II} complexes. ^{13}C NMR measurements show a non-fluxional 18S6 ligand in the complex while the platinum-195 NMR resonance at –4152 ppm indicates a mixed orientation of lone pair electrons on the sulfur donors.

Introduction

The complexation of both transition metal and main group metal ions by thiacrown ligands, such as 1,4,7-trithiacyclononane (9S3) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6), has been well researched over the past decade.[1−5] Complexes involving Pt^{II} and Pd^{II} with these macrocycles have been a particularly active area.[6−12] Such complexes are quite stable due to coordination of the soft metal center by the soft thioether ligand. The unique spectroscopic and electrochemical properties of crown thioether complexes containing the two divalent metal ions are a further impetus for research. Unusual d−d electronic transitions in the visible region result in atypical colors for both Pt^{II} (orange) and Pd^{II} (blue-green) complexes. Furthermore, the complexes exhibit a fully reversible M^{II}/M^{III} couple, observed in non-aqueous cyclic voltammetry; they also display fluxional trithioether ligands whose barriers of conversion are exceedingly small (near the limit of NMR detection of dynamic processes).[13] These physicochemical properties arise from the long M−S axial interactions between the metal ion and the sulfur donors of the thiacrown; long M−S interactions in solution have been correlated with the conformational preferences of individual crown thioether ligands.[14] Figure 1 shows the three distinct binding modes of thiacrowns to Pd^{II} and Pt^{II}, involving zero, one, and two long metal−sulfur interactions. These long interactions fall in the range 2.7−3.2 Å, which is longer than typical divalent palladium and platinum thioether sulfur bond lengths (2.3−2.4 Å), but less than the corresponding metal−sulfur Van der Waals distances.[15] Also, the electronic nature of these interactions is of considerable theoretical interest as they serve as intermediate cases between bonding and non-bonding situations.[16]

The initial report of the crystal structure of the complex $[Pt(9S3)_2](PF_6)_2$ revealed, surprisingly,[6] an elongated

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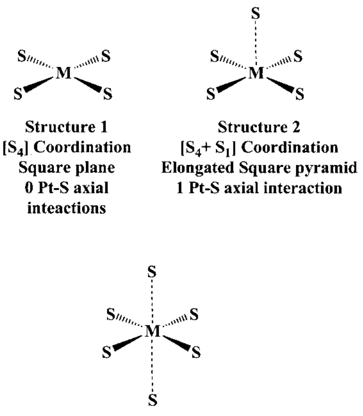

Structure 1
[S$_4$] Coordination
Square plane
0 Pt-S axial
inteactions

Structure 2
[S$_4$+ S$_1$] Coordination
Elongated Square pyramid
1 Pt-S axial interaction

Structure 3
[S$_4$+ S$_2$] Coordination
Elongated Octahedron
2 Pt-S axial interactions

Figure 1. Three coordination modes of d^8 metal ions displayed by thiacrowns

square pyramidal structure ([S$_4$ + S$_1$], Figure 1, Structure 2) rather than the more common, and anticipated, elongated octahedral structure ([S$_4$ + S$_2$], Figure 1, Structure 3). In the reported structure, the two 9S3 ligands were not centrosymmetrically bound to the Pt^{II}. One 9S3 was positioned *endodentate* to the metal ion while the second ligand was in an uncommon *exodentate* conformation. The *exodentate* conformation of 9S3 contrasts with that of the identical bis Pd^{II} analog.[8] Indeed, to the best of our knowledge, only one other *exodentate* binding case of 9S3 in a Pt^{II} structure has been reported.[17] Therefore, we undertook the current crystallographic study of the [Pt(9S3)$_2$]$^{2+}$ cation with various anions to see if this atypical 9S3 complex structure might be duplicated. The length of the axial sulfur–metal interaction serves as a sensitive probe for the examination of anion and solvent effects.[18a–18e] For example, dramatic solvent effects on Pd^{II} complexes containing thiacrown ligands have been reported for the analogous thiacrown 10S3 (1,4,7-trithiacyclodecane).[19,20] Interestingly, the linkage isomer obtained for the [Pd(10S3)$_2$]$^{2+}$ complex, reported by McAuley, has a six-membered chelate ring between the equatorial sulfurs, while our structure contains a five-membered chelate ring between the sulfurs. The switch in linkage isomer appears to be due to packing forces associated with a particular solvent (nitromethane vs. acetonitrile); this solvent–complex interaction has been confirmed via low temperature ^{13}C NMR studies. Similarly, macrocyclic hexathioether 18S6 complexes with Pd^{II} to form two different salts with different solid-state structures. The tetraphenylborate salt of [Pd(18S6]$^{2+}$ is yellow-brown while the hexafluorophosphate salt is green.[1,9] In addition, the Pd–S bond lengths and conformations of ethylene linkages also differ, illustrating how counterion effects can alter structures. As the spectroscopic and electrochemical properties of [Pt(18S6]$^{2+}$ have not been reported, those data are included here, along with our X-ray structure of the tetrafluoroborate salt.[9] Control of complex cation structure by solvent and counterion could have important implications in crystal engineering applications. Both Pd^{II} and Pt^{II} complexes of thiacrowns have been used by the Schröder and Lippolis groups as templates for control and the self-assembly of three-dimensional structures.[21,22]

Results and Discussion

Structures of [Pt(9S3)$_2$]$^{2+}$ Complexes

The tetrafluoroborates and hexafluorophosphates both crystallize in the monoclinic space group, *P*2$_1$/*c* (No. 14), while the triflate salt crystallizes in the orthorhombic space group, *Pbca* (No. 61). The asymmetric unit in all three lattices consists of the platinum(II) center, situated on an inversion center, one 9S3 ligand, one anion, and one nitromethane solvent molecule, each occupying general positions within the cell. For the hexafluorophosphate salt, both 9S3 ligands are centrosymmetrically bound to the Pt^{II} ion in the three structures (Figure 2), and the ligand shows an *endodentate* conformation with a [S$_4$ + S$_2$] coordination mode. There are four equatorial Pt–S bonds and two long distance Pt–S axial interactions forming an elongated octahedral structure. Notably, all three structures contrast with the prior structure of [Pt(9S3)$_2$](PF$_6$)$_2$, which shows one *exodentate* sulfur, non-centrosymmetrical binding of the two ligands, and no solvent molecules.[6] Our structural results, therefore, do not support the hypothesis that [S$_4$ + S$_1$] binding of 9S3 to Pt^{II} is its common and preferred coordination mode due to the conformation of the ligand.[11] Rather, packing effects, which depend upon the specific counterion and crystallization solvent, control whether [S$_4$ + S$_2$] or [S$_4$ + S$_1$] coordination is observed in structures of 9S3 and related macrocycles with d^8 metal ions such as Pt^{II} and Pd^{II}.

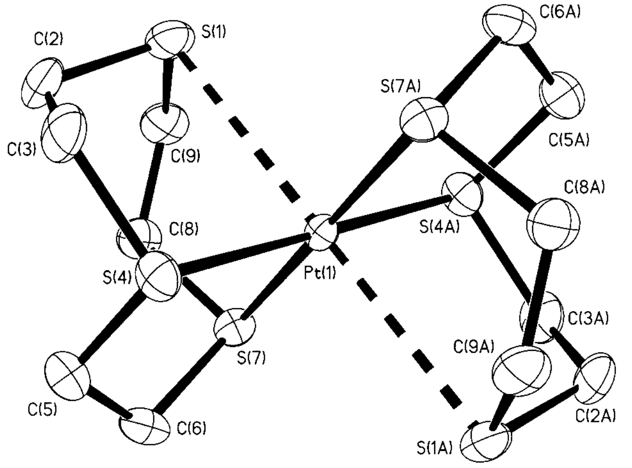

Figure 2. Thermal ellipsoid perspective (50% probability) of cation in [Pt(9S3)$_2$]](PF$_6$)$_2$·2 CH$_3$NO$_2$

Equatorial Pt–S bond lengths increase only very slightly, in the order BF$_4^-$ < PF$_6^-$ < OTf$^-$. Greater variation is seen, not unexpectedly, in the Pt–S axial distances, with the triflate showing a larger distance (over 0.1 Å) than the other two structures. However, the Pt–S distance is markedly greater, over 0.3 Å, than for the earlier $[Pt(9S3)_2](PF_6)_2$ structure − a dramatic effect arising from packing forces.[6] S−Pt−S chelate bite angles in the three structures are slightly less than 90°, with a commensurate expansion of the non-chelate angle to slightly above 90°. This effect is also seen in the $S_{equatorial}$−Pt−S_{axial} angles (Table 1), which are less than 90°, showing the axial sulfur bending towards the metal center.

Table 1. Selected bond lengths (Å) and angles (°) for $[Pt(9S3)_2](PF_6)_2\cdot 2CH_3NO_2$ (**1**), $[Pt(9S3)_2](BF_4)_2\cdot 2CH_3NO_2$ (**2**), $[Pt(9S3)_2](OTf)_2\cdot 2CH_3NO_2$ (**3**), and $[Pt(18S6)](BF_4)_2$ (**4**)

	1	2	3	4
Distances (Å)				
M−Seq	2.2923(8)	2.2901(1)	2.2962(16)	2.303(3)
	2.2939(9)	2.2927(1)	2.2987(15)	2.318(3)
				2.321(3)
				2.322(3)
M−Sax	3.072(8)	3.043(7)	3.185(7)	2.809(3)
M−S, exo	NA	NA	NA	4.099(3)
S−S, chelate	3.220(8)	3.214(7)	3.237(8)	3.250(3)
				3.230(3)
Angles, degrees				
S−M−S, chelate	89.20(3)	89.07(4)	89.58(6)	88.61(10)
				88.90(10)
S−M−S, non-chelate	90.80(3)	90.93(4)	90.42(6)	90.65(10)
				91.66(10)
S−M−S, axial	82.729(8)	82.906(4)	78.629(6)	84.23(10)
	84.265(8)	84.373(4)	80.458(6)	84.81(3)

Structure of $[Pt(18S6)]^{2+}$

The structure crystallizes in a triclinic cell with space group, $P\bar{1}$ (No. 2); Figure 3 shows a thermal ellipsoid perspective. The asymmetric unit consists of one $[Pt(18S6)]^{2+}$ cation and two BF_4^- anions, all occupying general positions within the cell. Note that, unlike the three 9S3 structures, there are no solvent molecules incorporated into the lattice. The 18S6 forms an elongated square pyramidal structure (Figure 1, Structure 2) with $[S_4 + S_1]$ coordination. One long Pt−S axial interaction is observed [2.809(3) Å], but the sixth sulfur donor is oriented *exodentate* to the Pt^{II} and at too great a distance [4.099(3) Å] to interact. Notably, our structure contrasts with the earlier $[Pt(18S6)]^{2+}$ structure with tetraphenylborate, which shows a symmetrical $[S_4 + S_2]$ binding of the 18S6.[9] As seen in the 9S3 structures, the coordination mode of the 18S6 can be switched between $[S_4 + S_2]$ and $[S_4 + S_1]$ depending upon crystal packing forces that arise from the counterion or crystallization solvent. Although the preferred conformation of the ligand is generally important in determining how it will bind to a metal ion, there appears to be some limited flexibility in coordination modes towards d^8 metal ions like Pt^{II} and Pd^{II}. For exclusively ethylene bridged thioether macrocycles like 9S3 and 18S6, the coordination mode can switch between $[S_4 + S_2]$ and $[S_4 + S_1]$, depending upon the solvent or anion. In that regard, our recent report of homoleptic Pt^{II} and Pd^{II} complexes of 12S3 (1,5,9-trithiacyclodecane, exclusive propylene bridges) shows examples of both $[S_4]$ and $[S_4 + S_1]$, but never $[S_4 + S_2]$ coordination.[10] The all-sulfur *exodentate* conformation of the12S3 ligand precludes its forming two Pt−S axial interactions, but it, too, has limited flexibility in its ability to coordinate these ions.

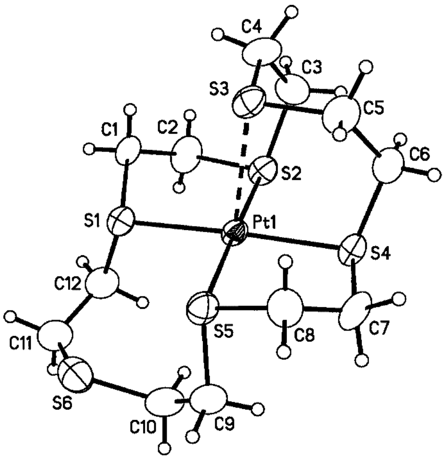

Figure 3. Thermal ellipsoid perspective (50% probability) of cation in $[Pt(18S6)](BF_4)_2$

The five-sulfur square pyramidal portion of the 18S6 ligand is in the eclipsed conformation, but strain within the macrocycle causes the remaining portion (involving the one *exodentate* sulfur atom) to adopt a staggered conformation. Previous 18S6 structures with Pd^{II} and Pt^{II} reported exclusively staggered or eclipsed conformers, so our structure represents an interesting intermediate case.[1,9] S−Pt−S chelate bite angles in the 18S6 structure are even smaller than the for the three 9S3 structures at slightly less than 89°. The four sulfur atoms in the equatorial plane (S1, S2, S4, and S5) are co-planar to within 0.126 Å. The Pt^{II} ion is displaced by 0.067(2) Å above the mean square plane and is directed towards the axial sulfur donor, S3. Equatorial distances are longer by 0.02 Å than in the earlier tetrafluoroborate structure, but the axial distance is surprisingly short. Indeed this is the shortest Pt−S axial distance observed in a homoleptic thioether complex of platinum(II). A full listing of Pt−S equatorial and axial distances for Pt^{II} thiacrown complexes that exhibit these two types of structures appears in Table 2. The two shortest Pt−S axial distances are observed, notably, for the two $[S_4 + S_1]$ structures, and both $[S_4 + S_1]$ structures show the platinum displaced towards the axial sulfur above the least-squares plane of the four sulfur donors. In general, the average Pt−S equatorial bond lengths show little variation, but there is a large difference in Pt−S axial distances.

Although there are no interionic contacts shorter than van der Waal's radii sums, there are interesting S···F contacts involving all six sulfur atoms, with distances ranging from 3.31(1) to 3.52(1) Å (average of 3.43(9) Å] − just outside the van der Waal's sum for sulfur and fluorine (S 1.80 Å; F 1.47 Å).[23] These contacts are roughly co-linear with the Pt−S bonds (range of Pt−S···F angles: 144(1)−175(1)°; average 166(11)°] and approximately along the line expected

Table 2. Listing of Pt−S equatorial and Pt−S axial distances for Pt^{II} thiacrown complexes that display $[S_4 + S_1]$ or $[S_4 + S_2]$ coordination

Complex	Anion	Solid state structure	Pt−S equatorial	Pt−S axial	Reference
$[Pt(9S3)_2]^{2+}$	PF_6^-	$S_4 + S_1$	2.29 Å	2.89 Å	[6]
$[Pt(18S6)]^{2+}$	BF_4^-	$S_4 + S_1$	2.32 Å	2.81 Å	this work
$[Pt(9S3)_2]^{2+}$	PF_6^-	$S_4 + S_2$	2.29 Å	3.07 Å	this work
$[Pt(9S3)_2]^{2+}$	BF_4^-	$S_4 + S_2$	2.29 Å	3.04 Å	this work
$[Pt(9S3)_2]^{2+}$	OTf^-	$S_4 + S_2$	2.30 Å	3.24 Å	this work
$[Pt(10S3)_2]^{2+}$	PF_6^-	$S_4 + S_2$	2.30 Å	3.21 Å	[11]
$[Pt(10S3)_2]^{2+}$	PF_6^-	$S_4 + S_2$	2.30 Å	3.23 Å	[14]
$[Pt(18S6)]^{2+}$	BPh_4^-	$S_4 + S_2$	2.30 Å	3.38 Å	[9]

for a lone-pair on fluorine (range of B−F···S angles: 127(1)−149(1)°; average 136(9)°], suggesting a weak donor−acceptor character of these interactions. Indeed, we observe very similar behavior in the tetrafluoroborate salt of $[Pt(9S3)_2]^{2+}$, which also has S···F contacts in the range 3.49(3)−3.61(3) Å, which are approximately co-linear with the Pt−S bonds (Pt−S···F angles: 165°−169°). In our hexafluorophosphate structure, we observe very short S···F contacts between the fluorides of the anion and the axial sulfur. At 3.191(8) Å, these are shorter than the van der Waal's sum. There is also a short contact between the axial sulfur and one oxygen of the nitromethane solvent at 3.34 Å. The two hexafluorophosphate structures of $[Pt(9S3)_2]^{2+}$ show noticeable differences in the nature of the S···F contacts. The previous structure shows one short S···F contact (3.43 Å) between the *exodentate* sulfur and a fluorine atom in one hexafluorophosphate anion.[6] A second fluorine in the same anion, *cis* to this first fluorine, links to an equatorial sulfur in a different cation at 3.23 Å. For the triflate structure, the anions and solvent lie along the open side of the complex cation, away from the axial sulfur position. We feel that the solid-state structures obtained for this series of compounds can be influenced by weak donor−acceptor interactions between the sulfur atoms of the thioether macrocycle and anions or solvent.

Spectroscopic and Electrochemical Measurements

A d−d electronic transition at 426 nm results in the orange color of the $[Pt(18S6)]^{2+}$ complex. The relatively small extinction coefficient confirms that this absorption band is a d−d transition. The analogous Pt^{II} complexes, $[Pt(9S3)_2]^{2+}$ and $[Pt(10S3)_2]^{2+}$, also show similar transitions near 430 nm.[8,11,14] Note that these three ligands are the ones whose complexes have the shortest platinum−sulfur axial interactions. When these strong axial interactions are not present, the color of the complex is dominated by the position of charge-transfer bands, and may range from yellow to colorless.[10,14]

Carbon NMR spectroscopy was undertaken on the 18S6 complex to see if there was evidence for fluxionality in solution, as observed for trithioether complexes of Pt^{II}. The $^{13}C\{^1H\}$ NMR spectra in two different solvents both show a simple three-line carbon spectrum consistent with a centrosymmetric binding of 18S6. There is little change in the appearance of the spectrum with temperature, even up to 150 °C, and so we do not see evidence for fluxionality of the coordinated 18S6 ligand. The simple NMR spectrum is not consistent with the $[S_4 + S_1]$ binding mode in the crystal structure, but rather the symmetrical $[S_4 + S_2]$ structure shown by the tetraphenylborate salt.[9] Our NMR spectroscopic data suggest that the ligand, in solution, forms an S-shaped elongated octahedral structure, and that packing effects during crystallization result in the $[S_4 + S_1]$ structure seen in our X-ray data. Another important result from the NMR study is the lack of fluxionality for the 18S6 ligand. Virtually every known 9S3 and 10S3 Pt^{II} complex shows fluxionality of the trithioether ligand. However, the 18S6 does not. The lack of fluxionality of the 18S6 may be due to the increased number of platinum−sulfur interactions (six vs. three) with the larger hexathioether macrocycle, supporting the 1,4-metallotropic shift exchange mechanism.[13]

Under the conditions of our cyclic voltammetry study, the complex $[Pt(18S6)]^{2+}$ exhibits an irreversible oxidation wave at +0.564 V and a second irreversible oxidation wave at +1.358 V. (both vs. Fc/Fc^+). Both are metal-centered oxidations and are assigned as a Pt^{II}/Pt^{III} couple and a Pt^{III}/Pt^{IV} couple, respectively. The electrochemical behavior resembles $[Pt(9S3)_2]^{2+}$ and $[Pt(10S3)_2]^{2+}$, but with two distinctions. First, the oxidation wave in the 18S6 complex appears at a higher positive potential, indicating greater difficulty in oxidizing the Pt^{II} center. Second, the +2/+3 couple for the trithioether complexes is fully reversible − not irreversible as observed for the 18S6 complex. We propose that the less flexible 18S6 cannot re-orient to facilitate oxidation of the Pt^{II}, thereby accounting for the greater difficulty of its oxidation and lack of reversibility in the electron transfer.

Lastly, the ^{195}Pt NMR spectrum of $[Pt(18S6)]^{2+}$ shows a single resonance at $\delta = -4152$ ppm, confirming the presence of a single complex in solution. The chemical shift is consistent with the hypothesis, regarding lone pair orientation on sulfur donors in macrocyclic thioether complexes,[10,12] that complexes with a mixed (half up, half down) orientation of lone pairs show values in the −4000 to −4300 ppm range, while those with all lone pairs on the sulfur donors oriented in the same direction have Pt resonances shifted upfield by ca. 500 ppm. Thus, the ^{195}Pt NMR chemical shift value agrees with the mixed lone pair orientation on the sulfur donors in the coordinated 18S6 ligand, as confirmed in our carbon-13 NMR work. We believe there is sufficient ^{195}Pt NMR spectroscopic data to establish a definite correlation between chemical shift and sulfur lone pair orientation in this series of complexes.

Conclusion

The crystal structures of four mononuclear Pt^{II} homoleptic complexes with two thiacrown ligands contrast with previous structural reports involving identical complex cations but differing anions or crystallization solvents. In the solid state, both [S_4 + S_1] and [S_4 + S_2] coordination of Pt^{II} by 9S3 and 18S6 are observed, depending upon packing forces. Our work illustrates how changes of counterion and solvent can have dramatic effects on the crystal structures for their complexes, suggesting that packing forces play a more dominant role than ligand conformation in determining specific solid-state structures. The spectroscopic and electrochemical properties of the complex [Pt(18S6)](BF_4)$_2$ are consistent with the presence of two Pt−S axial interactions in solution. The 18S6 ligand is non-fluxional in solution, in contrast to the trithiacrowns, and the ^{195}Pt NMR chemical shift indicates an alternating orientation of lone pair electrons on the sulfur donors.

Experimental Section

Materials: Thioether ligands 9S3 and 18S6, inorganic salts and K_2PtCl_4, and all solvents were purchased from the Aldrich Chemical Company, and used as received. The starting complex [$PtCl_2(C_2H_5CN)_2$] was prepared according to the literature method.[24]

Measurements: Elemental analyses were performed by Atlantic Microlab, Inc. of Atlanta, Georgia. Fourier transform infrared spectra were obtained using a Galaxy FT IR 5000 spectrophotometer and ultraviolet-visible spectra were obtained on a Varian DMS 200 UV/Visible spectrophotometer. ^{13}C{^{1}H} and ^{1}H NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CD_3NO_2 for both the deuterium lock and reference. ^{195}Pt{^{1}H} NMR spectra were recorded near 64.208 MHz using aqueous solutions of $[PtCl_6]^{2-}$ ($\delta = 0$ ppm) as an external reference and a delay time of 0.01 s. Referencing was verified versus authentic samples of $[PtCl_4]^{2-}$, which had a chemical shift at $\delta = -1626$ ppm, in agreement with its reported value of −1624 ppm.[25] A Biological Analytical Systems 50 Analyzer was used for all electrochemical measurements. The supporting electrolyte was 0.1 M $(Bu)_4NBF_4$ in CH_3CN, and sample concentrations were 1 mM. Voltammograms were recorded at a scan rate of 100 mV s^{-1}. The standard three-electrode configuration was as follows: platinum working electrode, Pt-wire auxiliary electrode, and Ag/AgCl reference electrode. All potentials were referenced against a Fc/Fc$^+$ couple.

Synthesis of $[Pt(9S3)_2]^{2+}$ Complex Salts

[Pt(9S3$_2$](BF$_4$)$_2$: A mixture of $K_2[PtCl_4]$ (100.8 mg, 0.243 mmol) and 1,4,7-trithiacyclononane (88.5 mg, 0.491 mmol) was boiled under reflux in a 2:1 methanol/distilled water solution (26 mL). The resultant brownish-orange reaction mixture was allowed to cool and was then partitioned into two equal volumes for the subsequent addition of counterion. $NaBF_4$ (56.3 mg, 0.513 mmol) was added to one aliquot and then cooled to 0 °C. Orange crystals thus formed were filtered off, washed with cold methanol (3 × 15 mL) and diethyl ether (3 × 15 mL) to yield bis(1,4,7-trithiacyclononane)platinum(II) tetrafluoroborate (76.2 mg, 86.3%). FT-IR (KBr): $\tilde{\nu}$ = 2980, 2935, 2832, 1427, 1401, 1320, 1285, 1225, 1165, 1061(s, BF_4^-), 834, 646, 526 cm^{-1}. $C_{12}H_{24}B_2F_8PtS_6$ (729.38): calcd. C 19.76, H 3.32, S 26.37; found C 19.99, H 3.25, S 26.25. Slow diffusion of diethyl ether into a nitromethane solution yielded X-ray quality crystals as a nitromethane solvate.

[Pt(9S3)$_2$](BPh$_4$)$_2$: $NaBPh_4$ (167.2 mg, 0.4886 mmol) was added to the remaining aliquot of $[Pt(9S3)_2]^{2+}$ and the resultant mixture chilled to 0 °C. The so-obtained dark orange crystals were then filtered off, washed with cold methanol (3 × 15 mL) and diethyl ether (3 × 15 mL) to yield bis(1,4,7-trithiacyclononane)platinum(II) tetraphenylborate (130 mg, 89.7%) as a dark orange solid. FT-IR (KBr): 3050, 2985, 1577, 1476, 1155, 746, and 608 cm^{-1}. Poor solubility of the complex in common solvents limited additional study. $C_{60}H_{64}B_2PtS_6$ (1194.25): calcd. C 60.34, H 5.40, S 16.11; found C 60.04, H 5.55, S 15.99.

[Pt(9S3$_2$](PF$_6$)$_2$: This compound has been previously reported, and a crystal grown from acetonitrile.[6] We were interested in repeating the crystallization using nitromethane. A mixture of $K_2[PtCl_4]$ (206 mg, 0.497 mmol) and 9S3 (195 mg, 1.00 mmol) were boiled under reflux in 2:1 methanol−water (v/v, 49 mL) solution for 19 h. The resulting yellow solution was filtered off and concentrated to 2/3 of its original volume. Upon addition of NH_4PF_6 (176 mg, 0.491 mmol), yellow crystals of the complex formed. After cooling to 0 °C, the crystals were filtered off, washed with cold methanol (3 × 15 mL), anhydrous diethyl ether (3 × 15 mL), and air-dried. The reaction produced bis(1,4,7-trithiacyclodecane)platinum(II) hexafluorophosphate (334 mg, 79.3%) as an orange crystalline solid. FT-IR (KBr): 2995, 2944, 2925, 2848, 1444, 1410, 1290, 1272, 932, 837 (s, PF_6^-), 558 cm^{-1}. The electronic absorption spectrum measured in acetonitrile showed three λ_{max}s, at 430 (ε = 120), 287 (ε = 11,000) and 250 nm (ε = 15,000), matching its literature spectrum.[6] Slow diffusion of diethyl ether into a nitromethane solution yielded X-ray quality crystals as a nitromethane solvate.

[Pt(9S3$_2$](OTf)$_2$: Silver triflate, AgOTf, $AgSO_3CF_3$ (277 mg, 1.08 mmol) was added to a solution of [$PtCl_2(C_2H_5CN)_2$] (193 mg, 0.513 mmol) dissolved in dichloromethane (3.5 mL) and propanenitrile (0.10 mL). This suspension was stirred vigorously for 5 h and the resultant white AgCl precipitate removed by filtration to yield a light yellow solution. The AgCl precipitate was then washed twice with additional CH_2Cl_2 (2 mL). 9S3 (200 mg, 1.11 mmol) was quickly added and stirred overnight. If too much time lapses before the addition of the 9S3 ligand, the Pt solution turns blue, evidently due to the formation of an aqua complex.[24] Diethyl ether was then added drop-wise to precipitate orange crystals of [Pt(9S3$_2$](OTf)$_2$ (129 mg, 29.6% yield). $C_{14}H_{24}F_6O_6PtS_8$ (853.90): calcd. C 19.69, H 2.83; found C 19.61, H 2.86. The visible electronic absorption spectrum measured in acetonitrile showed one λ_{max} at 420 nm (ε = 110). Slow diffusion of diethyl ether into a nitromethane solution yielded X-ray quality orange prismatic crystals as a nitromethane solvate. The crystals readily desolvate in air, but are quite stable when protected.

Synthesis of $[Pt(18S6]^{2+}$ Salts

A mixture of $K_2[PtCl_4]$ (315 mg, 0.759 mmol) and 18S6 (278 mg, 0.771 mmol) was boiled under reflux in a methanol−water (2:1 v/v, 84 mL) solution for 17.5 h. The resulting yellow solution was filtered and then concentrated to 40 mL. Four 10 mL portions of the solution were then divided and used for subsequent anion metathesis reactions.

[Pt(18S6](BF$_4$)$_2$: An aliquot of the [Pt(18S6]$^{2+}$ solution (10 mL) was mixed with NaBF$_4$ (42.2 mg, 0.384 mmol), and the resultant solution filtered. Slow evaporation of the filtrate yielded crystals (36.0 mg, 26.0% yield) of 1,4,7,10,13,16-hexathiacyclooctadecaneplatinum(II) tetrafluoroborate suitable for X-ray diffraction studies. IR (KBr): 2990, 2945, 2844, 1427, 1320, 1285, 1234, 1177, 1075−1033 (s, BF$_4^-$), 925, 808, 656, 574, 564 cm^{-1}. $C_{12}H_{24}B_2F_8PtS_6$ (729.38): calcd. C 19.76, H 3.32, S 26.37; found C 20.04, H 3.27, S 26.18.3

[Pt(18S6](PF$_6$)$_2$: An aliquot of the [Pt(18S6]$^{2+}$ solution (10 mL) was mixed with NH$_4$PF$_6$ (59.5 mg, 0.365 mmol), and the solution was chilled in an ice bath for 1.5 hours to afford light orange crystals that were filtered off and washed with chloroform (5 mL) to yield 1,4,7,10,13,16-hexathiacyclooctadecaneplatinum(II) hexafluorophosphate (126 mg, 78.4%) as an orange crystalline solid. IR (KBr): 2991, 2952, 2850, 1430, 1285, 1244, 1180, 1077, 1056, 841 (s, P−F), 651, 574, 558 cm^{-1}. $C_{12}H_{24}P_2F_{12}PtS_6$ (845.70): calcd. C 17.04, H 2.86, S 22.75; found C 17.15, H 2.85, S 22.66. As this salt offered the best solubility properties, most solution work was performed on it. The electronic absorption spectrum measured in acetonitrile showed two λ_{max}s, at 426 nm (ε = 84) and at 235 (ε = 28222). The electrochemistry of the complex showed one irreversible oxidation wave at +564 mV and a second irreversible oxidation wave at +1358 mV vs. Fc/Fc$^+$. ^{1}H NMR (300 MHz, CD$_3$CN, 25 °C): broad, poorly resolved resonances from 2.8 to 3.6 ppm. ^{13}C{^{1}H} NMR (75 MHz, CD$_3$CN, 25 °C): three peaks of approximately equal intensity at 27.54, 38.86, and 42.59 ppm. These were all confirmed to be methylene resonances by a DEPT experiment. ^{195}Pt{^{1}H} NMR (64.4 MHz, CD$_3$NO$_2$, 25 °C), δ ($v_{1/2}$): singlet at δ = −4152 ppm (91 Hz).

[Pt(18S6](BPh$_4$)$_2$: The synthesis and X-ray structure of this compound has been reported previously.[1] An aliquot of the [Pt(18S6]$^{2+}$ solution (10 mL) was mixed with NaBPh$_4$ (131 mg, 0.383 mmol), and the solution was then chilled in an ice bath for 1.5 hours to give light orange crystals that were filtered off and washed with chloroform (5 mL) to yield 1,4,7,10,13,16-hexathiacyclooctadecaneplatinum(II) tetraphenylborate (55.0 mg, 24.7%). IR (KBr): 3090, 3050, 2993, 2954, 1430, 1285, 1244, 1180, 1077, 1056, 750, 750, 670, 574 cm^{-1}. The electronic absorption spectrum measured in acetonitrile matched the reported literature spectrum.[1]

[Pt(18S6](ClO$_4$)$_2$: An aliquot of the [Pt(18S6]$^{2+}$ solution (10 mL) was mixed with NaClO$_4$ (53.9 mg, 0.440 mmol), and the solution was allowed to slowly evaporate to afford light orange crystals that were filtered off. These crystals were then washed with chloroform (5 mL) to yield 1,4,7,10,13,16-hexathiacyclooctadecaneplatinum(II) perchlorate (32.0 mg, 22.3%). IR (KBr): 2981, 2945, 2914, 1430, 1285, 1094−1074 (s, ClO$_4^-$), 925, 777, 623, 574 cm^{-1}. $C_{12}H_{24}Cl_2O_8PtS_6$ (754.68): calcd. C 19.10, H 3.21, Cl 9.40, S 25.44; found C 19.18, H 3.19, Cl 9.45, S 25.57. ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO, 25 °C): three broad peaks of approximately equal intensity at δ = 25.8, 27.2, and 40.7 ppm.

Caution! Although the perchlorate salt prepared in this report did not appear to be shock-sensitive, they should always be handled with caution and used only in very small quantities.

X-Ray Data Collection and Processing

Suitable crystals of all complexes were grown by slow diffusion of diethyl ether into a nitromethane solution. Table 3 summarizes the key crystallographic details for the structures.

9S3 Complexes: For the tetrafluoroborate and hexafluorophosphate structures, intensity data were collected at low temperature

Table 3. Crystallographic data summary for [Pt(9S3)$_2$](PF$_6$)$_2$·2CH$_3$NO$_2$ (**1**), [Pt(9S3)$_2$](BF$_4$)$_2$·2CH$_3$NO$_2$ (**2**), [Pt(9S3)$_2$](OTf)$_2$·2CH$_3$NO$_2$ (**3**), and [Pt(18S6)](BF$_4$)$_2$ (**4**)

	1	**2**	**3**	**4**
Empirical formula	$C_{14}H_{30}F_{12}P_2N_2O_4S_6Pt$	$C_{14}H_{30}F_8B_2N_2O_4S_6Pt$	$C_{16}H_{30}F_6N_2O_{10}S_8Pt$	$C_{12}H_{24}B_2F_8S_6Pt$
fw, amu	967.9	851.47	975.99	729.38
Size/mm	0.44 × 0.34 × 0.17	0.34 × 0.29 × 0.10	0.48 × 0.14 × 0.12	0.36 × 0.27 × 0.11
Appearance	orange prisms	orange prisms	orange prisms	yellow, parallelepiped
Space group	monoclinic	monoclinic	orthorhombic	triclinic
Crystal system	$P2_1/c$	$P2_1/c$	*Pbca*	$P\bar{1}$
a (Å)	9.9379(15)	9.5710(12)	14.024(3)	5.463(2)
b (Å)	15.310(2)	15.227(19)	11.353(2)	10.436(2)
c (Å)	10.0017(15)	9.7031(12)	20.665(4)	10.094(7)
α (°)	90	90	90	93.22(2)
β (°)	99.587(2)	102.178(3)	90	94.34(3)
γ (°)	90	90	90	90.99(3)
V (Å)^3	1500.5(4)	1382.3(3)	3290.4(11)	1083.7(6)
Z	2	2	4	2
$\rho_{calcd.}$ (g cm^{-3})	2.142	2.046	1.970	2.235
Radiation [λ (Å)]	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	5.203	5.609	4.854	7.118
Trans. coeff.	0.2028 and 0.4660	0.2515 and 0.5985	0.2040 and 0.5935	0.657 and 1.000
T (K)	193(2)	193(2)	173(2)	293(2)
Refls. collected	8593	7369	26774	4038
Refls. unique	3538	3119	2969	3807
R index[a] [$I > 2\sigma(I)$]	$R1$ = 0.0327	$R1$ = 0.0340	$R1$ = 0.0445	$R1$ = 0.0457
R indices[a] (all data)	R1= 0.0371 $wR2$ = 0.0930	$R1$ = 0.0462 $wR2$ = 0.1175	$R1$ = 0.0504 $wR2$ = 0.0964	$R1$ = 0.0729 $wR2$= 0.1343

[a] $R1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; with $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

on a Siemens SMART 1 K CCD diffractometer[26,27] equipped with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods,[26] and refinement was done using full-matrix least-squares techniques (on F^2). Structure solution, refinement and the calculation of derived results were performed with the SHELXTL[28] package of computer programs. For the triflate structure, intensity data were measured at room temperature with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) on a Rigaku AFC-8 diffractometer[29,30] equipped with a 1 K mercury CCD detector.

18S6 Complex: Intensity data were measured at room temperature with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) on a Rigaku AFC7R diffractometer. Data were corrected for Lorentz and polarization effects, and for absorption, using semi-empirical methods. The structure of the 18S6 complex was solved by direct methods and refined by using full-matrix least-squares techniques (on F^2). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in optimized positions ($d_{\mathrm{C-H}} = 0.96$ Å) with assigned thermal parameters equal to 120% of the U_{eq} value of their host atom. Structure solution, refinement and the calculation of derived results were performed with the SHELXTL[28] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber,[31a] and the real and imaginary anomalous dispersion corrections were those of Cromer.[31b]

CCDC-219803 (for $[\mathrm{Pt(9S3)_2}](\mathrm{PF_6})_2\cdot 2\mathrm{CH_3NO_2}$), -219804 (for $[\mathrm{Pt(9S3)_2}](\mathrm{BF_4})_2\cdot 2\mathrm{CH_3NO_2}$), -238122 (for $[\mathrm{Pt(9S3)_2}](\mathrm{OTf})_2\cdot 2\mathrm{CH_3NO_2}$) and -238123 (for $[\mathrm{Pt(18S6)}](\mathrm{BF_4})_2]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] A. J. Blake, M. Schröder, in *Advances in Inorganic Chemistry* (Ed.: A. G. Sykes), vol. 35, Academic Press, Inc., New York, **1990**, 2.

[2] S. R. Cooper, *Acc. Chem. Res.* **1988**, *21*, 41.

[3] S. R. Cooper, S. C. Rawle, *Structure and Bonding (Berlin)* **1990**, *72*, 1.

[4] M. Schröder, *Pure and Appl. Chem.* **1988**, *60*, 517.

[5] W. N. Setzer, E. L. Cacioppo, Q. Guo, G. J. Grant, D. D. Kim, J. L. Hubbard, D. G. VanDerveer, *Inorg. Chem.* **1990**, *29*, 2672.

[6] A. J. Blake, R. O. Gould, A. J. Holder, T. I. Hyde, A. J. Lavery, M. O. Odulate, M. Schröder, *J. Chem. Soc., Chem. Commun.* **1987**, 118.

[7] A. J. Blake, A. J. Holder, G. Reid, M. Schröder, *J. Chem. Soc., Dalton Trans.* **1994**, 627.

[8] A. J. Blake, A. J. Holder, T. I. Hyde, Y. V. Roberts, A. J. Lavery, M. Schröder, *J. Organomet. Chem.* **1987**, *323*, 261.

[9] A. J. Blake, R. O. Gould, A. J. Lavery, M. Schröder, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 274.

[10] G. J. Grant, A. M. Goforth, D. G. VanDerveer, W. T. Pennington, *Inorg. Chim. Acta* **2004**, *357*, 2107.

[11] A. J. Blake, R. D. Crofts, M. Schröder, *J. Chem. Soc., Dalton Trans.* **1993**, 2259.

[12] A. J. Blake, Y. V. Roberts, M. Schröder, *J. Chem. Soc., Dalton Trans.* **1996**, 1885.

[13] H. Nikol, H.-B. Bürgi, K. I. Hardcastle, H. B. Gray, *Inorg. Chem.* **1995**, *34*, 6319.

[14] G. J. Grant, N. S. Spangler, W. N. Setzer, D. G. VanDerveer, *Inorg. Chim. Acta* **1996**, *246*, 41.

[15] T. W. Hambley, *Inorg. Chem.* **1998**, *37*, 3767.

[16] The sum of the van der Waals radii is 3.50 Å for platinum(II) and sulfur and 3.40 Å for palladium(II) and sulfur. J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry*, 4th edition, Harper Collins: New York, **1993**, 292.

[17] M. A. Bennett, A. J. Canty, J. K. Felixberger, L. M. Rendina, C. Sunderland, A. C. Willis, *Inorg. Chem.* **1993**, *32*, 1951.

[18] Over twenty structures of 9S3 coordinated to $\mathrm{Pt^{II}}$ are known. For a few examples, see: [18a] G. J. Grant, I. M. Poullaos, D. F. Galas, D. G. VanDerveer, J. D. Zubkowski, E. J. Valente, *Inorg. Chem.* **2001**, *40*, 564. [18b] G.-H. Lee, *Acta Crystallogr., Sect. C* **1998**, *54*, 906. [18c] G. J. Grant, C. G. Brandow, D. F. Galas, J. P. Davis, W. T. Pennington, J. D. Zubkowski, E. J. Valente, *Polyhedron* **2001**, *20*, 3333. [18d] G. J. Grant, I. M. Poullaos, D. F. Galas, S. C. Carter, D. G. VanDerveer, *J. Chem. Soc., Dalton Trans.* **2002**, 2973. [18e] G. J. Grant, D. F. Galas, D. G. VanDerveer, *Polyhedron* **2002**, *21*, 879. [18f] G. J. Grant, S. M. Carter, I. M. Poullaos, A. L. Russell, D. G. VanDerveer, *J. Organomet. Chem.* **2001**, *637–639*, 683. [18g] G. J. Grant, J. D. Pool, D. G. VanDerveer, *Dalton Trans.* **2003**, 3981.

[19] S. Chandrasekhar, A. McAuley, *Inorg. Chem.* **1992**, *30*, 2663.

[20] G. J. Grant, K. A. Sanders, W. N. Setzer, D. G. VanDerveer, *Inorg. Chem.* **1991**, *30*, 4053.

[21] A. J. Blake, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, M. Schröder, *Crystal Engineering* **1999**, *2*, 153.

[22] A. J. Blake, L. M. Gilby, R. O. Gould, V. Lippolis, S. Parsons, M. Schröder, *Acta Crystallogr., Sect. C* **1998**, *54*, 295.

[23] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[24] V. Y. Kukushkin, A. Oskarsson, L. I. Elding, *Inorg. Syntheses* **1997**, *31* 279.

[25] P. S. Pregosin (Ed.) in *Transition Metal Nuclear Magnetic Resonance*, Elsevier: New York, **1991**, 251, and references cited therein.

[26] Programs used for data collection, solution and refinement of this structure were: *SMART 5.054, SAINT+ 6.01, SHELXTL 5.1*, **1998–1999**, Bruker AXS, Madison, WI, USA.

[27] SADABS, R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

[28] *SHELXTL 5.1*, **1998–1999**, Bruker AXS, Madison, WI, USA.

[29] *CrystalClear*; Rigaku/MSC, The Woodlands, TX, USA, **1999**.

[30] R. A. Jacobson, REQAB, subroutine of *CrystalClear*; Rigaku/MSC, The Woodlands, TX, USA, **1999**.

[31] [31a] D. T. Cromer, J. T. Waber, *International Tables for X-ray Crystallography*, vol. IV, Table 2.2B, The Kynoch Press, Birmingham, England, **1974**. [31b] D. T. Cromer, *International Tables for X-ray Crystallography*, vol. IV, Table 2.3.1, The Kynoch Press, Birmingham England, **1974**.

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