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Synthesis and Structure of $[NBu_4][Pt_2Ag(\mu\text{-}SC_4H_8)_2(C_6F_5)_6]$, a Trinuclear Compound Displaying Two Structurally Different Anions in the Solid State

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The result of the reaction between $[NBu_4][Pt(C_6F_5)_3(tht)]$ (tht = SC_4H_8, tetrahydrothiophene) and $AgClO_4$ in CH_2Cl_2 is a trinuclear anionic complex which has been isolated in the form of its tetrabutylammonium salt $[NBu_4][Pt_2Ag(\mu\text{-}tht)_2(C_6F_5)_6]$ (**1**). $Pt_2AgC_{60}F_{30}H_{52}NS_2$ is triclinic, space group $P\bar{1}$, with $a = 13.486(3)$ Å, $b = 14.697(4)$ Å, $c = 17.333(4)$ Å, $\alpha = 106.01(2)°$, $\beta = 90.50(2)°$, $\gamma = 98.03(3)°$, V = 3262.4(13) Å, and $Z = 2$. As a unique proof of the concerted nature of the electronic effects operating at the aceptor silver center, the asymmetric unit contains two independent half-anions (lying on centers of inversion) with different bond distances in their cores: anion **1a**, Pt–Ag = 2.783(1) Å and Ag–S = 2.778(2) Å; anion **1b**, Pt–Ag = 2.862(1) Å and Ag–S = 2.547(2) Å. ^1H and ^{19}F NMR spectra point to dynamic behavior in solution of the complex anion.

Introduction

Earlier work in our laboratory[1] has established that anionic perhalophenylplatinate complexes behave as Lewis bases and react with silver salts or complexes to afford polynuclear complexes displaying donor–acceptor Pt→Ag bonds. The strength of the Pt→Ag interactions seems to be simultaneously dependent on the basicity of the anionic platinate fragment, the acidity of the silver center (modulated by the other ligands attached to it in each case), and some additional interactions between silver and ortho-X atoms in the C_6X_5 ligands (X = F, Cl) of the platinate complex, as suggested by the structures and properties of several systems of this class.[2–7] However, no two cases are mutually identical and even the more similar ones (as for instance,[2] $(C_6F_5)_4$-Pt→Ag(tht) (**A**) and $(C_6F_5)_2(C_6Cl_5)_2$Pt→Ag(tht) (**B**)) do not permit absolute comparisons between bond distances and donor–acceptor behavior, since the basicity of the platinum centers is likely to be different in **A** or **B** due to differences between the C_6F_5 and the C_6Cl_5 groups and to the existence of four Ag···*o*-F contacts in **A** and two Ag···*o*-F and two Ag···*o*-Cl contacts in **B**.[8]

In this paper we report the synthesis and structural characterization of $[NBu_4][Pt_2Ag(\mu\text{-}tht)_2(C_6F_5)_6]$ (**1**), whose trinuclear anion exists in two diferent geometries in the same crystal, thereby enabling for the first time a direct comparison between interactions at the silver center.

Experimental Section

C, H, and N analyses and conductance measurements were performed as described elsewhere.[2] IR spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 833 spectrophotometer from Nujol mulls between polyethylene sheets. NMR spectra were obtained on Varian XL200 and Unity 300 spectrometers. $[NBu_4][Pt(C_6F_5)_3tht]$ was prepared as described elsewhere.[9] Tetrahydrothiophene (tht) was from Fluka and its purity was determined by ^1H NMR spectroscopy and mass spectrometry. All the reactions in which a silver reagent was used were carried out under exclusion of light.

Safety Note. Perchlorate salts with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with great caution.

Synthesis of $[NBu_4][Pt_2Ag(\mu\text{-}tht)_2(C_6F_5)_6]$. To a solution of $[NBu_4]$-$[Pt(C_6F_5)_3tht]$ (0.23 g, 0.23 mmol) in 30 mL of CH_2Cl_2 was added an equimolar amount of $AgClO_4$ (0.047 g, 0.23 mmol), and the mixture was stirred at room temperature for 4 h. A quantity of unreacted $AgClO_4$ which remained in suspension was filtered off, and the resulting solution was evaporated to dryness; the oily residue was treated with 60 mL of OEt_2 to separate the NBu_4ClO_4 as an insoluble white solid. The resulting solution was evaporated to dryness, and white solid $[NBu_4][Pt_2Ag(\mu\text{-}tht)_2(C_6F_5)_6]$ was obtained (79% yield). Analysis Found (Calcd) : C, 37.33 (37.55); H, 2.80 (2.71); N, 0.57 (0.72). Λ_M $(Me_2CO)^{10}$ = 155 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): C_6F_5, 1635 m, 1607 w, 1346 m, 1096 s, 1058 vs, 958 vs, 950 vs, 802 s, 787 m, 776 s; tht, 1260 m.

Preparation of Crystals for X-ray Structure Determination. Suitable crystals for X-ray purposes were obtained by slow diffusion of n-hexane into a solution of 0.03 g of $[NBu_4][Pt_2Ag(\mu\text{-}tht)_2(C_6F_5)_6]$ in CH_2Cl_2 (4 mL) at –30 °C.

X-ray Structure Analysis. The heterotrinuclear complex $[(C_6F_5)_3Pt(\mu\text{-}tht)Ag(\mu\text{-}tht)Pt(C_6F_5)_3]^-$ crystallizes as the tetra-n-butylammonium salt in space group $P\bar{1}$ with $Z = 2$. The structure was determined using well established techniques. A platelike crystal, mounted on the tip of a glass fiber with epoxy cement, was used for geometric and intensity data collection. Four-circle diffractometer data were taken at two temperatures, –40 °C and 20 °C.[12] The crystal data given in Table I and

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[●] Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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(8) See ref 1 Table I.

(9) Usón, R.; Forniés, J.; Martinez, F.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1980**, 888.

(10) The molar conductivity has been calculated by assuming that the anion $[Pt_2Ag(\mu\text{–}tht)_2(C_6F_5)_6]^-$ is not dissociated, and the resulting value is sligthtly beyond the high end of the expected range for a 1:1 electrolyte.[11] However, if it assumed that the trinuclear anion is completly dissociated into $[Pt(C_6F_5)_3tht]^-$ and Ag^+, the molar conductivity would be 77 Ω^{-1} cm^2 mol^{-1}, a value lower than that expected for a 1:1 electrolyte.

(11) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(12) Room temperature crystal data: Data collection was performed at 20 °C. $a = 13.533(2)$, $b = 14.854(2)$, $c = 17.341(3)$ Å, $\alpha = 105.86(1)°$, $\beta = 90.71(1)°$, $\gamma = 98.08(1)°$, $V = 3314.8(9)$ Å^3, $Z = 2$; size 0.5 × 0.4 × 0.1 mm^3; $\lambda = 0.71073$ Å; μ(Mo Kα) = 46.5 cm-1; absorption correction (DIFABS);[24] four-circle diffractometer, Siemens/Stoe AED2; $4 < 2\theta < 48°$; $2\theta/\omega$ scan method; Total number of reflections 9290; 5778 reflections with $F_o^2 \geq 3\sigma(F_o^2)$; heavy-atom method; refinement on F to $R = 0.0382$, $R_w = 0.0411$; all atoms treated as anisotropic; weighting scheme $w^{-1} = \sigma^2(F_o) + 0.0016F_o^2$; 869 variables. Selected bond lengths (Å) and angles (deg): Pt(1)–Ag(1), 2.801(1); Pt(2)–Ag(2), 2.874(1); Ag(1)–S(1), 2.739(3); Ag(2)–S(2), 2.545(3); Pt(1)–S(1), 2.319(3); Pt(2)–S(2), 2.295(3); Pt(1)–Ag(1)–S(1), 49.59(1); Pt(2)–Ag(2)–S(2), 49.7(1); Ag(1)–Pt(1)–S(1), 63.9(1); Ag(2)–Pt(2)–S(2), 57.7(1); Pt(1)–S(1)–Ag(1), 66.7(1); Pt(2)–S(2)–Ag(2), 72.7(1).

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Table I. Crystallographic Data for $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$

formula	$Pt_2AgC_{60}H_{52}$-$NF_{30}S_2$	V, Å^3	3262.4(13)
formula weight	1919.21	Z	2
space group	$P\bar{1}$	ρ_{calc}, g/cm^3	1.94
a, Å	13.486(3)	μ(Mo Kα), cm^{-1}	47.6
b, Å	14.697(4)	diffractometer	Siemens/ STOE AED2
c, Å	17.333(4)	radiation	Mo Kα (λ_α = 0.71073 Å)
α, deg	106.01(2)	temperature, °C	–40 ± 1
β, deg	91.50(2)	transmission coeff	0.467–1.000
γ, deg	98.03(3)		
R^a	0.0492		
$R_w{}^b$	0.0731		

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = [\sigma^2(|F_o|) + 0.0035|F_o{}^2|]$.

Table II. Selected Bond Distances (Å) and Angles (deg) for $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]^a$

1a		1b	
	Bond Distances		
Pt(1)–Ag(1)	2.783(1)	Pt(2)–Ag(2)	2.862(1)
Ag(1)–S(1)	2.778(2)	Ag(2)–S(2)	2.547(2)
Pt(1)–S(1)	2.326(2)	Pt(2)–S(2)	2.294(2)
Pt(1)–C(1)	2.022(6)	Pt(2)–C(23)	2.025(6)
Pt(1)–C(7)	2.072(8)	Pt(2)–C(29)	2.079(8)
Pt(1)–C(13)	2.082(9)	Pt(2)–C(35)	2.071(8)
Ag(1)···F(14)	2.717(6)	Ag(2)···F(36)	2.805(5)
	(ρ = 1.37)		(ρ = 1.41)
	Bond Angles		
Pt(1)–Ag(1)–S(1)	49.4(1)	Pt(2)–Ag(2)–S(2)	49.8(1)
Ag(1)–Pt(1)–S(1)	65.2(1)	Ag(2)–Pt(2)–S(2)	58.0(1)
Pt(1)–S(1)–Ag(1)	65.4(1)	Pt(2)–S(2)–Ag(2)	72.3(1)
C(19)–S(1)–C(22)	94.8(5)	C(41)–S(2)–C(44)	97.5(4)
S(1)–Pt(1)–C(1)	175.3(2)	S(2)–Pt(2)–C(23)	170.3(2)
C(7)–Pt(1)–C(13)	174.6(3)	C(29)–Pt(2)–C(35)	174.9(3)
C(1)–Pt(1)–C(7)	88.6(3)	C(23)–Pt(2)–C(29)	89.8(3)
C(7)–Pt(1)–S(1)	95.1(2)	C(29)–Pt(2)–S(2)	91.7(2)
S(1)–Pt(1)–C(13)	87.7(2)	S(2)–Pt(2)–C(35)	91.2(2)
C(1)–Pt(1)–C(13)	88.9(3)	C(23)–Pt(2)–C(35)	88.1(3)
S(1)–C(19)–C(20)	104.0(10)	S(2)–C(41)–C(42)	103.6(8)
C(19)–C(20)–C(21)	111.6(12)	C(41)–C(42)–C(43)	113.0(9)
C(20)–C(21)–C(22)	110.8(11)	C(42)–C(43)–C(44)	112.4(10)
C(21)–C(22)–S(1)	103.7(10)	S(2)–C(43)–C(44)	106.9(9)

[a] The interaction parameter ρ is defined as $\rho = d_{AB}/r_A + r_b$ in which the covalent radii r are taken from ref 18.

the distances and angles in Table II are taken from the low-temperature structure determination. The diffractometer data in both cases were corrected for slow decay, which was observed in the time-dependent changes of the intensities of three monitor reflections. For the low-temperature data, a measured absorption correction was applied, based on 10 complete Ψ-scans of reflections with diffractometer angle χ near 90° and also on measurements of 252 reflections and their symmetry equivalents. While one doubt about the structure had to be resolved (vide infra), the refinement came to an otherwise uneventful conclusion. In the final least-squares refinement, 9200 data with $F_o{}^2 \geq 2\sigma(F_o{}^2)$ were used to fit 869 parameters, for a data-to-parameter ratio of 10.6. Routine computations were performed on VAX/VMS systems with the SHELX-TL-PLUS[13] program package. Table I summarizes the crystallographic data and least-squares residuals for the low temperature structure.

Pseudosymmetry in the crystal structure led us to undertake a more careful analysis of the structural results. In order to be able to present a clear picture of the questions that we wished to explore and of our resolution of these questions, we present here a brief description of the overall structure. The $NBu_4{}^+$ cations sit on a set of general equivalent positions, and the two independent complex anions lie across two centers of inversion related by $[0,{}^1/_2,{}^1/_2]$. The two anions are parallel to each other, and the conformations of the peripheral C_6F_5 ligands are essentially identical. The only differences between the two anions arise in the sulfur-bridged Pt–Ag core and are the following: (a) The two independent Pt–Ag bond lengths are 2.783(1) and 2.862(1) Å, and the corresponding Ag–S distances are 2.778(2) and 2.547(2) Å, respectively. Thus, one anion has a considerably shorter Pt–Ag bond, and a considerably longer Ag–S bond, than the other. (b) The tht ligands have different conformations in the two anions, and are disposed differently with respect to the rest of the anion in each case.

We conducted a series of detailed tests on the structural results, using the room-temperature data, as described in the following. The usual tests for a false least-squares minimum all led us to the same original structural results. These tests included adding atoms to the model in different orders, moving atoms away from the positions found (thus to establish different starting points for refinement), and undertaking refinements beginning with two identical molecules as starting points. All of these attempts converged to the same results.

We were thus prompted to consider more thoroughly the possiblity that the cell we were using was really A-centered and that the two bond-length differences were artifacts of having conducted a least-squares refinement in an incorrect cell. Adding more interest to these considerations was the fact that the central N-atom of the cation is at a position quite close to $[{}^1/_2,{}^1/_4,{}^3/_4]$—which would be a center of symmetry (requiring disorder, which we did not observe) in the space group $A\bar{1}$.

The extended crystal structure comprises alternating planes of oppositely charged ions. The trinuclear anion sits in the *bc*-plane with adjacent entities centered at [000] and $[0,{}^1/_2,{}^1/_2]$. The $NBu_4{}^+$ cations lie on the plane $x = {}^1/_2$, with adjacent entities located at $[{}^1/_2,{}^1/_4,{}^3/_4]$ and $[{}^1/_2,{}^3/_4,{}^1/_4]$. This arrangement leaves most of the ions with similar environments in the crystal. The one difference in environment between the crystallographically independent complex anions is that the nearest cationic groups are differently oriented in the two cases. That is, successive $NBu_4{}^+$ moieties in the plane $x = {}^1/_2$ are related to each other by centers of symmetry and thus do not present the same space-filling properties to their surroundings.

An oscillation photo of [011] showed very weak reflections on the odd layers —so weak as to leave their nature (e.g., Bragg or superlattice scattering) in doubt. The $(k + l)$ odd reflections in the intensity data are quite weak and poorly represented. (A supplementary table shows how the $(k + l)$ odd data measure up against data from other index classes.) A crude test of the possibility of an incorrect cell was simply to make the transformation and delete what were the $(k + l)$ odd data of the original cell. This gave results which were not acceptable. The residuals came out 3–4 times higher than in the original refinement, and the atoms of the important groups were poorly resolved. This result in itself could suffice to establish the correct cell, but we preferred to conduct more tests in order to obviate the possibility of a perjured structure.

We conducted a peak-shape analysis on $(k + l)$ odd and $(k + l)$ even data. Superlattice reflections would be expected to have systematically different profiles from those of normal Bragg reflections. In our case, the two groups give roughly equivalent peak-shape parameters. (Traces of learned profiles for $(k + l)$ odd and $(k + l)$ even data are available as supplementary material.) This result, along with the fact that the environments of the two anions are not identical, led us to the conclusion that the original cell and space group are correct. Indeed, since we did not observe what would have been a required disorder for the butyl groups of the cation (if the original cell were wrong), we observe that the closest contacts between atoms of the cation and those of the anion are different for the two independent anions.

We conducted one further test of the structure. A development and refinement of the structure was done using all data and refining on $F_o{}^2$—a procedure which is especially effective in identifying and resolving pseudosymmetry problems.[14] The results of this came out in excellent accord with those obtained (and reported here) by traditional methods.

Results and Discussion

Synthesis. $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$, **1** (79% yield), was prepared by addition of $AgClO_4$ to a CH_2Cl_2 solution of $[NBu_4][Pt(C_6F_5)_3tht]$ in 1:1 ratio. Although the reaction requires a 1:2 (Ag:Pt) molar ratio (eq 1) we have observed that a better yield can be obtained if the process is carried out in 1:1 molar ratio. The excess of $AgClO_4$ remains insoluble after the reaction time and can be easily eliminated.

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(13) Siemens Analytical X-Ray Instruments, Inc., SHELXTL-PLUS Software Package, Release 4.11/V, Madison, Wisconsin, 1990.

(14) Sheldrick, G. M., SHELXL-92, FORTRAN program for the refinement of crystal structures, beta test version, 1992.

$$\mathrm{AgClO_4 + 2[NBu_4][Pt(C_6F_5)_3(tht)] \xrightarrow{CH_2Cl_2/OEt_2} [NBu_4][Pt_2Ag(\mu\text{-}tht)_2(C_6F_5)_6] + NBu_4ClO_4} \quad (1)$$

On the other hand, when $[NBu_4][Pt(C_6Cl_5)_3tht]$ is reacted with $AgClO_4$, in order to obtain the analogous pentachlorophenyl derivative (1:1 molar ratio, 3 h, room temperature), partial decomposition takes place and $[Pt_2(\mu\text{-tht})_2(C_6Cl_5)_4]$, **2**,[15] is the only product identified, albeit in very low yield (26%). Complex **2** seems to be formed through a trans-arylation process (eq 2) which is not unprecedented in this type of reaction.[2]

$$\mathrm{2[NBu_4][Pt(C_6Cl_5)_3(tht)] + 2AgClO_4 \xrightarrow{CH_2Cl_2/OEt_2} [Pt_2(\mu\text{-}tht)_2(C_6Cl_5)_4] + 2NBu_4ClO_4 + 2AgC_6Cl_5} \quad (2)$$

If the reaction is carried out with a 2:1 molar ratio, a mixture which contains most of the unreacted starting material and **2** is recovered after 1.5 h.

The reaction between $[NBu_4][Pt(C_6F_5)_3py]$ or $[NBu_4][Pt(C_6F_5)_3(BzNH_2)]$ and $AgClO_4$ under similar conditions—conducted with the intention of preparing analogous trinuclear complexes but without any covalent bridging ligand supporting the Pt–Ag bonds—renders pale yellow solids whose NMR spectra (^{19}F and ^1H) indicate that in both cases a mixture of several unidentified compounds is present.

On the other hand, the reaction between **1** and $BzNH_2$ in CH_2Cl_2 (molar ratio 1:2) results in the formation of a white solid whose NMR ^{19}F and ^1H spectra indicate the presence in the mixture of $[Pt(C_6F_5)_3tht]^-$ and $[Ag(BzNH_2)_2]^+$; i.e., the reaction produces, as expected, the cleavage of the Pt(μ-tht)Ag bond system.

NMR. The ^1H NMR spectrum of $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$ in CD_2Cl_2 at −80 °C shows two broad signals at 3.13 (4-H) (α-CH_2) and 1.83 (4-H) ppm (β-CH_2) due to tht and signals due to NBu_4^+: 2.98 (8-H) (α-CH_2–); 1.48 (8-H) (β-CH_2–); 1.28 (8-H) (γ-CH_2–); 0.89 (12-H, –CH_3) ppm.

The ^{19}F NMR spectra of $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$ in CD_2Cl_2 at −80 °C and at room temperature are identical, and show the following signals: F_o, −117.13 (4-F, $J_{Pt-F_o} = 363.8$ Hz), −117.80 (2-F, $J_{Pt-F_o} = 512.6$ Hz); F_m, −163.68 (4-F), −165.29 (2-F); F_p, −162.26 (2-F), −164.01 (1-F) ppm. This indicates the presence of two inequivalent types of C_6F_5 group (2:1) with a typical spin system AA′MM′X for each group. The ^{19}F NMR spectrum of $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$ in CD_2Cl_2 at room temperature undergoes a systematic change upon addition of $[NBu_4][Pt(C_6F_5)_3tht]$. The pattern remains similar, but the chemical shifts of all signals are changed, with the signals due to the C_6F_5 group *trans* to tht suffering more significant modifications than the others. No signals due to free $[Pt(C_6F_5)_3tht]^-$ are observed. This fact indicates that equilibrium dissociative processes are present and the simple processes in eq 3 could represent the experimental findings.

$$\begin{array}{l} \mathrm{[Pt_2Ag(\mu\text{-}tht)_2(C_6F_5)_6]^- \rightleftharpoons [PtAg(\mu\text{-}tht)(C_6F_5)_3] + [Pt(C_6F_5)_3(tht)]^-} \\ \qquad\qquad\qquad\qquad\qquad \Updownarrow \\ \qquad\qquad\qquad\qquad \mathrm{[Pt(C_6F_5)_3(tht)]^- + Ag^+} \end{array} \quad (3)$$

This dynamic behavior has been observed as well in the ^1H NMR (CD_2Cl_2) spectrum. The ^{19}F NMR spectrum of $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$ in acetone shows that similar dynamic processes are present in this solvent too; no signals corresponding to $[NBu_4][Pt(C_6F_5)_3tht]$—which would result from complete dissociation of the trinuclear complex in this donor solvent—are observed.

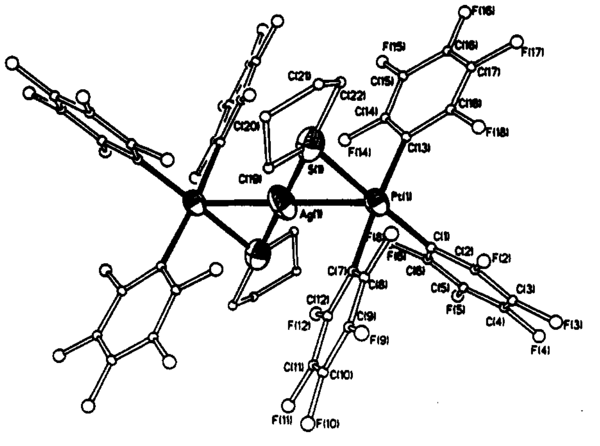

Figure 1. Drawing of anion **1a** from the crystal structure of $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$, showing the atom labeling scheme. Heavy atoms are represented by their 50% probability ellipsoids.

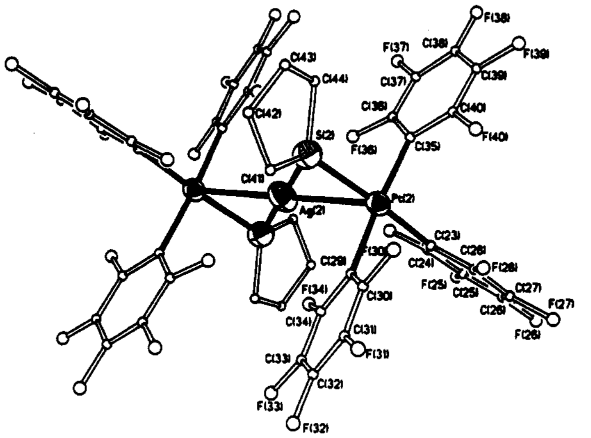

Figure 2. Drawing of anion **1b** from the crystal structure of **1**. Heavy atoms are represented by their 50% probability ellipsoids.

Structural Characterization of the Complex $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$ (1). There are two independent and perceptibly different anions $[Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]^-$ per unit cell (**1a**, **1b**). The structures of the two anions with the atom naming schemes are shown in Figures 1 and 2. Selected bond distances and angles are given in Table II.

As can be seen from Figures 1 and 2, the two anions are basically the same but with small, although significant, differences. In each case the anion consists of two "$Pt(C_6F_5)_3tht$" units joined by a silver atom. The silver atom is located on an inversion center so that there are two half-anions in the crystallographic asymmetric unit. Each "$Pt(C_6F_5)_3tht$" fragment is connected to the silver center through Pt→Ag and S→Ag donor→acceptor bonds. The Pt–C and Pt–S distances are very similar in the two anions and lie within the range found in other platinum pentafluorophenyl derivatives.[2,16,17] However, the platinum silver vector makes a different angle with the perpendicular to the basal plane in the two anions (24.5(2)° **1a** and 31.9(1)° **1b**) and the Pt–Ag and Ag–S distances are rather different as well in the two cases.

The Pt–Ag distances (2.783(1) Å **1a**, 2.862(1) Å **1b**) are in the range of distances found in other pentafluorophenyl platinum–silver complexes.[1] Some examples have been described for which shorter Pt–Ag distances have been found $\{[(tht)(C_6F_5)_3PtAg(PPh_3)]$ (2.637(1) Å),[16] $[(tht)(C_6F_5)_2(C_6Cl_5)PtAg(PPh_3)]$ (2.650(2) Å),[2] $[(C_6F_5)_4PtAg(tht)]^-$ (2.641(1) Å),[2] [*cis*-$(C_6F_5)_2(C_6Cl_5)_2PtAg(tht)]^-$ (2.692(2) Å)[2]$\}$. It must be pointed out that in

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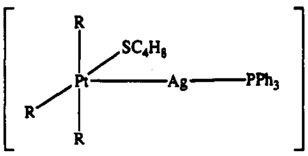
Chart I



all these cases the silver center is essentially dicoordinated, the Pt→Ag bond being totally unsupported by any covalent bridging ligand and the Pt→Ag vector is perpendicular to the basal platinum plane, a situation for which a better overlap of the d_{z^2} platinum orbital with the adequate empty orbitals of the silver center is obtained. All these facts militate toward the formation of stronger Pt→Ag donor–acceptor bonds.

As far as the Ag–S distances are concerned, the corresponding one in anion **1b** (Ag(2)–S(2)) is 2.547(2) Å, similar to Ag–S bridging distances (2.554 and 2.520 Å) found in $[Ag(\mu\text{-tht})(tht)]BF_4$,[18] a compound containing bridging and terminal tetrahydrothiophene. However, the distance found in anion **1a** (Ag(1)–S(1)) is 2.778(2) Å, thus indicating a perceptibly weaker Ag–S interaction in this case.

The Pt–S–Ag angles are 65.4(1)° (**1a**) and 72.3(1) (**1b**) and are in the range of $M(\mu\text{-tht})M'$ angles found in complexes containing M–M′ bonds supported by the tht ligand.[19–23]

The tht ligands have different conformations and are disposed differently with respect to the rest of the anions in each case. The angles formed by the SC_2 (i.e. the plane defined by the sulfur and the two adjacent C atoms of the SC_4H_8 ligand) and the PtAgS planes are 71.4° (**1a**) and 87.7° (**1b**). There is a subtle disorder as is often seen in tht and thf ligands, as indicated by the anisotropic displacement parameters of β- and β'- C atoms.

As we have observed in the structures of related compounds, in the present structure one C_6F_5 ring of each Pt-centered fragment is oriented in such a way as to permit short *o*-F···Ag contacts.[8]

Concluding Remarks

It is worthwhile to compare the structure of the anions in **1** with that of $[Pt(C_6F_5)_3thtAgPPh_3]$, which is obtained by reacting the same platinate substrate $[Pt(C_6F_5)_3tht]^-$ with $O_3ClOAgPPh_3$.[16] In this case (Chart I) the silver center which is already bonded to PPh_3 interacts with the $[Pt(C_6F_5)_3tht]^-$ fragment through only a Pt→Ag bond (2.637(1) Å), which is perpendicular to the basal plane, and no interaction between the S and Ag atoms is observed.

In the present case (**1**), however, the naked Ag^+ cation is forced to interact with two $[Pt(C_6F_5)_3tht]^-$ units in order to obtain at least dicoordination. To achieve this end, one of the alternatives represented in Chart II would be adequate, but seemingly neither the platinum center in the mononegative $[(C_6F_5)_3Pt(tht)]^-$ fragment nor the S atom (already coordinated to Pt) in the neutral SC_4H_8 ligand is able to donate enough electron density to satisfy the requirements of the bare Ag^+ cation. Some rearrangement is necessary to increase the electron density at the silver center and this can be achieved in two different forms (Chart III) which significantly differ in both bond distances and angles.

Chart II

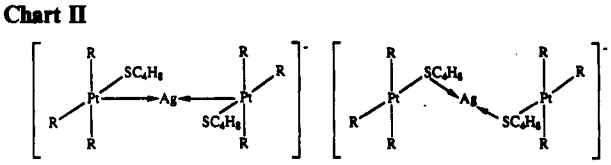
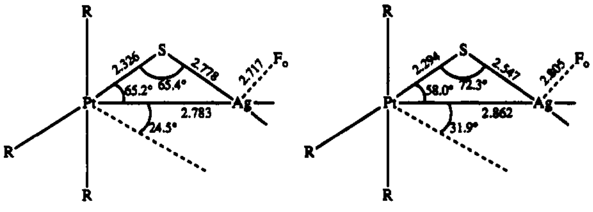


Chart III



1a **1b**

The following features are noteworthy:

(a) The Pt–Ag bonds are not perpendicular to the platinum basal plane but form angles of 24.5(2)° (**1a**) or 31.9°(1) (**1b**) with the perpendicular (dotted line to Pt).

(b) The Pt–Ag and S–Ag distances are qualitatively inversely correlated: 2.783(1) and 2.778(2) Å (**1a**) in comparison with 2.862(1) and 2.547(2) Å (**1b**).

(c) This is the result of several changes: an opening of the Pt–S–Ag angle (from 65.4(1)° to 72.3(1)°) and a closing of the S–Pt–Ag angle (from 65.2(1)° to 58.0(1)°), by ≈6° in each case.

(d) The structure of the bridging SC_4H_8 rings (not represented in Chart III) is somewhat irregular but not disordered. The plane SC_2 (defined by the S atoms and the two adjacents C atoms) forms with the PtSAg plane at distinctly different angles: 71.4° in **1a** and 87.7° in **1b**.

(e) Finally, each half-anion (Chart III) displays a Ag···*o*-F contact (two contacts in the whole anion) which also changes from 2.717(6) (**1a**) to 2.805(5) Å (**1b**).

Summarizing, we see a local electroneutrality effect operating at the acidic silver center on all the potentially donor centers on a concerted form. The existence of two different anions in the same crystal seems to be the response of a flexible molecule to its surroundings in the crystalline state. After solving the structure at room temperature,[12] we took a new set of data at low temperature (see Table I) in order to determine whether a slight change in the magnitude of the packing forces would lead to changes in the geommetries of the molecular cores. No chemically significant changes were noted. The data used in this paper correspond to the low temperature determination.

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Supplementary Material Available: For the crystal structure of $[NBu_4][Pt_2Ag(\mu\text{-tht})_2(C_6F_5)_6]$ at two temperatures, full tables of crystal data, anisotropic displacement parameters, and full tables of bond distances and angles, and at room temperature summary of diffraction intensities as a function of index class and traces of learned profiles for $(k + l)$ odd and $(k + l)$ even data (19 pages). Ordering information is available on any current masthead page.

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