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Synthesis and characterization of new allyl palladium complexes with thionate ligands; X-ray molecular structures of $[Pd_3(\eta^3\text{-}C_4H_7)_3\{pm(Me)_2S\}_2](CF_3SO_3)$ and $[Pd\{pm(Me)_2S\}_2]$, $\eta^3\text{-}C_4H_7 = \eta^3\text{-2-Me–}C_3H_4$, $pm(Me)_2S$ = Pyridine-4,6-dimethyl-2-thionate

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Abstract

The reaction of $[Pd(\eta^3\text{-}C_4H_7)]CF_3SO_3$ ($\eta^3\text{-}C_4H_7 = \eta^3\text{-2-MeC}_3H_4$) (**1**), prepared in situ by reaction of $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ with $AgCF_3SO_3$, with various thionate ligands, gives new polymeric complexes formulated as $[Pd(\eta^3\text{-}C_4H_7)(RS)]_n$ (**2**) [RS = pyS (pyridine-2-thionate)], im(Me)S(imidazole-3-methyl-2-thionate) (**3**), pm(Me)$_2$S (pyrimidine-4,6-dimethyl-2-thionate) (**4**). A solution of **4** contaminated with KCF_3SO_3 evolves to give crystals that correspond to a new polymeric species whose X-ray crystal molecular structure indicates the presence of cationic infinite chains built of trinuclear units, $[Pd_3(\eta^3\text{-}C_4H_7)_3\{pm(Me)_2S\}_2]^+$ (**5**). Finally, the formation of a mononuclear thionate-containing palladium complex $[Pd\{pm(Me)_2S\}_2]$ (**6**) occurs from a solution of **5** after prolonged periods. An X-ray crystal structure determination indicates a square-planar disposition of two thionate ligands around the Pd atom. The different complexes were characterized by spectroscopic techniques. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Palladium complexes; Thionate; Allyl; Pyridine-4,6-dimethyl-2-thionate; Pyridine-2-thionate; Imidazole-3-methyl-2-thionate

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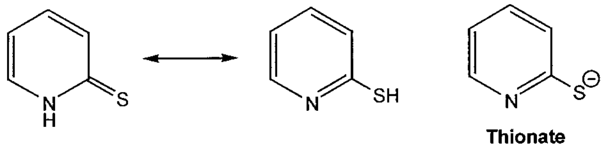
1. Introduction

Heterocyclic thionates are ligands derived from heterocyclic thiones that contain at least one deprotonated heterocyclic thioamide group $(N–C–S)^-$ (see Chart 1) [1] and can act as monodentate, chelating and bridging ligands. The aforementioned systems have been extensively studied in the field of coordination chemistry [2]. After the preparation of the first complex, $[RuCl(pyS)(PPh_3)_2]$ (pyS = pyridine-2-thionate) [3], several families of thionate-containing late transition metal complexes have been described, most of which are regarded as polynuclear species with *S*,*N*-bridging ligands, although in recent years other coordinating modes of these ligands have been established [4]. With regard to Group 10 metals, several thionate-containing complexes of palladium have been prepared [5] and, in



(Chart 1)

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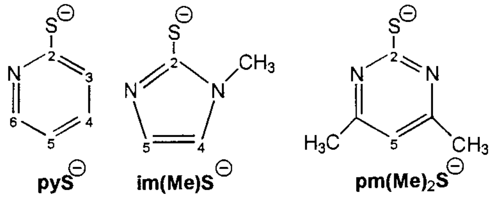
particular, Deeming et al. [6] have prepared some hetero- and homopolynuclear species whose X-ray crystal structures reveal the presence of thionate ligands, such as pyridine-2-thionate (pyS) and pyridine-6-methyl-2-thionate (pyMeS), acting as *S*,*N*-bridging ligands. Following the studies on the early transition metallocenes, some of us recently prepared [7] a family of pyrimidine-4,6-dimethyl-2-thionate containing zirconocene complexes, $Cp_2Zr(X)(pm(Me)_2S)$ (X = alkyl, alkynyl, hydride), and in the work described here we have considered the reactivity of the synthon $[Pd(\eta^3\text{-}C_4H_7)]^+$ toward some thionate ligands. This study has allowed the synthesis and characterization of new allyl palladium complexes with thionate ligands.

2. Results and discussion

Complexes **2**–**4** were obtained by addition of the potassium salt of the appropriate thionate to a dichloromethane solution of $[Pd(\eta^3\text{-}C_4H_7)]CF_3SO_3$ (**1**), $(\eta^3\text{-}C_4H_7) = (\eta^3\text{-2-Me–}C_3H_4)$, which is formed by reaction of the dimer $[\{Pd(\eta^3\text{-}C_4H_7)Cl\}_2]$ and the salt $AgCF_3SO_3$ in dichloromethane (Scheme 1).

The complexes are air-stable, both in the solid state and in solution, and the solids, orange for **2** and yellow for **3** and **4**, are soluble in common polar organic solvents.

A dichloromethane solution of **4** contaminated with KCF_3SO_3 was concentrated in order to obtain crystals of this compound but, surprisingly, crystals of a new complex were isolated as the only characterized compound. We have confirmed the formation of **5** as the only characterised compound when to a CH_2Cl_2 solution of a pure sample of **4** was added KCF_3SO_3 in (1:1) molar ratio. This compound corresponds to a polymeric chain composed of cationic trinuclear units, $[Pd_3(\eta^3\text{-}C_4H_7)_3\{pm(Me)_2S\}_2]^+$ (**5**) (vide infra). As yet we cannot put forward any plausible explanation for the formation of this compound from the polymeric species **4**. Deeming et al. [6b] described the molecular trinuclear species $[Pd_3(\eta^3\text{-}C_4H_7)_3(pyS)_2](ClO_4)$. For this complex an arrangement of three square-planar Pd(II) atoms linked by two μ_3-pyS ligands was proposed by analogy with the related complex $[Pd_3(dmp)_3(pyS)_2](BF_4)$ [dmp = 2-(dimethylaminomethyl)phenyl], whose X-ray molecular structure had been determined. However, the polymeric complex **5**, obtained from **4**, is structurally quite different than that prepared by Deeming et al. (see discussion below).



Scheme 1.

Finally, when CH_2Cl_2 solutions of **5** were kept for 2 week periods, crystals of a new mononuclear species, $[Pd\{pm(Me)_2S\}_2]$ (**6**), were isolated, although the process of its formation is unknown. It seems reasonable that the formation of the square-planar complex containing two thionate chelate ligands is termodynamically favored. Several species of this stoichiometry for Pd(II) have been reported previously [5c].

The new species have been characterized by elemental analysis, mass spectrometry, IR spectroscopy and ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy. The mass spectral analysis of **2** showed a peak at $m/z = 760$, and the abundance of the signals corresponds to the trinuclear species of stoichiometry $[Pd_3(\eta^3\text{-}C_4H_7)_2(pyS)_3]^+$, resulting from the loss of an allyl group from the neutral species $[Pd(\eta^3\text{-}C_4H_7)(pyS)]_3$. Additional signals corresponding to the loss of both an allyl and pyS groups ($m/z = 650$) from the trinuclear neutral species and the dimer fragment $[Pd(pyS)]_2^+$ ($m/z = 434$) were also observed. However, for complex **5** the most representative peak in the mass spectrum appears at $m/z = 462$, corresponding to the cationic fragment $[Pd_2(\eta^3\text{-}C_4H_7)_2\{\mu\text{-pm(Me)}_2S\}]^+$. The mass spectral data are not conclusive in terms of assignment of the grade of nuclearity of these complexes, although for complex **2** a trinuclear structural disposition could be tentatively considered (vide infra). ^1H- and $^{13}C\{^1H\}$-NMR spectra for complexes **2**–**5** indicate that they exhibit a fluxional behaviour in solution and such behaviour was observed in different deuterated solvents, namely CD_3CN, $CDCl_3$ and $(CD_3)_2CO$. Tables 1 and 2 show the values for the ^1H resonances, H–H coupling constants and ^{13}C resonances for the different complexes.

Room temperature ^1H-NMR spectrum of complex **2** in $(CD_3)_2CO$ exhibits a unique set of resonances for symmetrical allyl groups with three signals corresponding to H (*syn*), H (*anti*) and the methyl group, along with the resonances for the pyridine ring of a unique type of thionate ligand. The $^{13}C\{^1H\}$-NMR spectrum in $CDCl_3$ also exhibits the resonances for a symmetrical allylic group with a broad resonance at $\delta = 61.5$ for the two terminal carbon atoms. These results are indicative of a fluxional behaviour of the complex in solution, which would render equivalent the different allyl and thionate groups of the structure. In the solid state, on the basis of the mass spectral data, a static structure containing bridging pyS groups through the N and S atoms of the thionate ligand can be postulated (see Fig. 1).

Spectroscopic data for complexes **3** and **4** are also indicative of a fluxional behaviour for these complexes in solution, in a similar way to that previously described for complex **2**. Single, broad or complex signals, depending of the nature of the deuterated solvent employed at room temperature, corresponding to the allyl and thionate (imidazole-3-methyl-2-thionate for **3** and pyrimidine-4,6-dimethyl-2-thionate for **4**) are present in their ^{1}H- and ^{13}C{^{1}H}-NMR spectra (see experimental data in Tables 1 and 2). A static polynuclear structure in the solid state, containing bridging im(Me)S and pm(Me)$_2$S ligands, may be also proposed for complexes **3** and **4**, respectively. Complex **5** also exhibits a fluxional behaviour in solution and a variable ^{1}H-NMR study was carried out. At low temperature (-90°C) broad signals, which would correspond to three sets of unsymmetrical allyl and thionate ligands, were observed. When the temperature was raised (-30°C) well resolved signals (singlets and doublets), which correspond to three sets of unsymmetrical allyl units appear, whereas the spectrum at 45°C shows resonances for a single type of symmetrical allyl group, indicating that all allyl groups had become equivalent.

On the basis of these results, a static polynuclear structure with three sets of unsymmetrical allyl ligands with bridging pyrimidine-4,6-dimethyl-2-thionate units may be considered for complex **5** in the solid state and also in solution at low temperature. However, in solution, when the temperature is raised, a rearrangement process probably occurs through the breaking of the Pd–N bond of the thionate ligand, giving rise to the allyl and thionate ligand equivalents. In order to gain a better insight into the nature of **5** an X-ray crystal structure study was carried out.

The crystal structure of **5** is made up of infinite chains formed by trinuclear cations $[Pd(\eta^3\text{-}C_4H_7)_3\{pm(Me)_2S\}_2]^+$ crossing the crystal down the *y*-direction, and of $[CF_3SO_3]^-$ anions and water molecules intercalated between organometallic chains. The presence of these chains constitutes the original feature of the structure. In fact, in all other known trinuclear complexes with pyridine- or benzothiazole-2-thiolates (S–N) the homo- or heterometallic cations (Rh, Ir, Ag, Pd) form discrete trimetallic units [6,10]. These trinuclear species result from addition of the electrophilic synthon ML^+ to the dinuclear M_2(S–N)$_2$ neutral complexes. An intramolecular coordination of the third metallic centre through the sulfur atoms is allowed by simple changes in conformation (high fluxionality) of the dinuclear metalloligand. The nature of this fluxionality may be altered with our bulkier dimethyl substituted pm(Me)$_2$S ligand, forcing an intermolecular coordination of the third [Pd(allyl)]$^+$ fragment. The structure of the trimetallic cation present in the asymmetric unit of the $P2_1/c$ space group is shown in Fig. 2(a) together with the simplified model of its growth upon the trimolecular extension through coordination of the Pd3 atom (Fig. 2(b)) on sulfur atoms.

The major difference between our open (chain) structure and that containing a discrete trimetallic framework, as described by Deeming [6b], concerns the Pd···Pd distances. Our shortest Pd···Pd vector (Pd1–Pd2), with a value of 3.616(1) Å, is longer than the three Pd···Pd distances (close to 2.95 Å) reported

Table 1
^{1}H-NMR data for complexes **2**–**6**

Complex		2-Me–C_3H_4			Thiolate[a]
		CH_3	H_{anti}	H_{syn}	
2[b]		2.01 (s, 3H)	2.82 (s, 2H)	3.54 (s, 2H)	7.44 (d, H_3, $J_{HH}=10$), 7.23 (t, H_4, $J_{HH}=8$), 6.73 (t, H_5, $J_{HH}=8$), 8.15 (d, H_6, $J_{HH}=18$)
3[c]		2.08 (s, 3H)	2.49 (br, 2H)	3.83 (br, 2H)	6.44 (s, H_4 and H_5), 3.49 (s, 3H, CH_3)
4		2.08 (br, 3H)[b,c], 2.04 (br, 3H)[d]	2.99 (br, 2H)[b,c], 2.91 (br, 2H)[d]	3.93 (br, 2H)[b,c], 3.66 (br, 2H)[d]	6.61[b] (s, H_5), 6.76[c] (s, H_5), 6.55[d] (s, H_5), 2.33[b] (s, 6H, 2CH_3), 2.31[c] (s, 6H, 2CH_3), 2.27[d] (s, 6H, 2CH_3)
5	Allyl 1	2.22 (s, 3H)	2.99 (s, 2H), 3.25 (s, 2H)	3.96 (s, 2H), 4.34 (s, 2H)	2.43, 2.32 (br, CH_3), 6.98, 6.89 (br, H_5)
	Allyl 2	2.19 (s, 3H)	2.93 (s, 2H), 3.31 (s, 2H)	3.81 (s, 2H), 4.31 (s, 2H)	
	Allyl 3	2.15 (s, 3H)	3.17 (s, 2H), 3.71 (s, 2H)	4.10 (s, 2H), 4.21 (s, 2H)	
6[b]					2.35(s, 12H), 6.68 (s, 2H_5)

[a] J = coupling constants in Hz.

[b] $(CD_3)_2CO$.

[c] $CDCl_3$.

[d] CD_3CN.

Table 2
$^{13}C\{^1H\}$-NMR data for complexes **2**–**4**

Complex	2-Me–C_3H_4			Thiolate
	–CH_3	C_1, C_2	C_3	
2[a]	23.61	61.54	112.33	191.33 C_2, 129.22 C_3, 118.10 C_4, 134.53 C_5, 149.92 C_6
3[b]	23.83	52.17 broad, 64.54 broad	Not observed	35.10 –CH_3, 120.37 C_4, 127.58 C_5, C_2 not observed
4[a]	23.60	59.40	112.32	23.56 –CH_3, 165.97 C_2, 126.65 C_4, C_6, 113.94 C_5
6[a]				23.82 –CH_3, 166.05 C_2, 127.02 C_4, C_6, 114.21 C_5

[a] $CDCl_3$.
[b] $(CD_3)_2CO$.

for the discrete trimetallic cation. However, as in other trinuclear structures, the pm(Me)$_2$S ligand behaves as a triply bridging ligand.

The loss of allyl ligands from **5** upon prolonged standing in solution, leads to the mononuclear inorganic complex Pd{pm(Me)$_2$S}$_2$ (**6**). The ^1H- and $^{13}C\{^1H\}$-NMR spectra of this compound show the characteristic resonances of a chelate pyridine-4,6-dimethyl-2-thionate unit (see Tables 1 and 2). An X-ray structure analysis of **6** shows that the Pd atoms lie on the symmetry centres of the *C*2/*c* space group (Fig. 3). The separation of planar molecules (3.48 Å) corresponds roughly to that between two π-systems. The presence of some electronic communication between the 16 electron Pd centres (filled d_{z2}, empty p_z atomic orbitals) cannot be ruled out.

In conclusion, we have studied the reactivity of the electrophilic fragment [Pd(η^3-C_4H_7)](CF_3SO_3) (**1**) towards different thionate ligands, and as a result a number of polymeric complexes that probably contain bridging thionate groups have been isolated. In solution the isolated compounds exhibit a fluxional behaviour, which was detected by NMR spectroscopy.

3. Experimental

3.1. General conditions

All manipulations and reactions were carried out using standard Schlenk-line techniques under dinitrogen. All solvents were freshly distilled from appropriate drying agents and degassed before use.

The compound [{Pd(η^3-C_4H_7)(μ-Cl)}$_2$] [8] and the potassium salts of the appropriate thionates K(pyS), K[im(Me)S] and K[pm(Me)$_2$S] [9] were prepared as described in the literature. $AgCF_3SO_3$ was purchased from Aldrich.

Elemental analyses were performed with a Perkin–Elmer 2400 microanalyzer. IR spectra were recorded as KBr pellets in the region 4000–200 cm^{-1} with a Perkin–Elmer PE 883 IR spectrometer. Mass spectra were recorded on a VG autospec instrument using the FAB technique. NMR spectra were recorded on a Varian Unity FT-300 spectrometer [300 MHz (^1H) and 75 MHz (^{13}C)] or a Varian-Gemini FT-200 spectrometer [200 MHz (^1H) and 50 MHz (^{13}C)].

3.2. Synthesis of complex 2

To a solution of [{Pd(η^3-C_4H_7)(μ-Cl)}$_2$] (0.110 g, 0.280 mmol) in 25 ml of CH_2Cl_2, $AgCF_3SO_3$ (0.146 g, 0.560 mmol) was added. The solution was stirred at room temperature overnight and protected from light. The white precipitate of AgCl was then filtered off, and to the yellow solution was added [K(PyS)] (0.100 g, 0.670 mmol). The solution was allowed to stir for 6 h and after concentration a white precipitate of KCF_3SO_3 was formed which was filtered off. The resulting yellow solution was then concentrated and Et_2O was added to obtain **2** as a yellow solid, which was dried under vacuum. Yield: 0.097 g. (53%). Anal. Found: C, 39.74; H, 4.38; N, 4.76%. $C_9H_{11}NPdS$. Calc.: C, 39.79; H, 4.05; N, 5.15%.

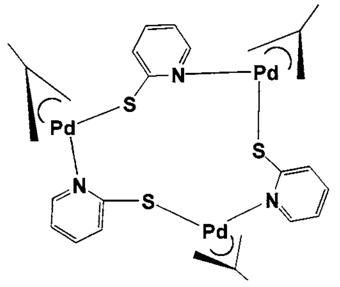


Fig. 1. A postulated static structure, in the solid state, of **2** containing pyS groups through the N and S atoms of the thionate ligand.

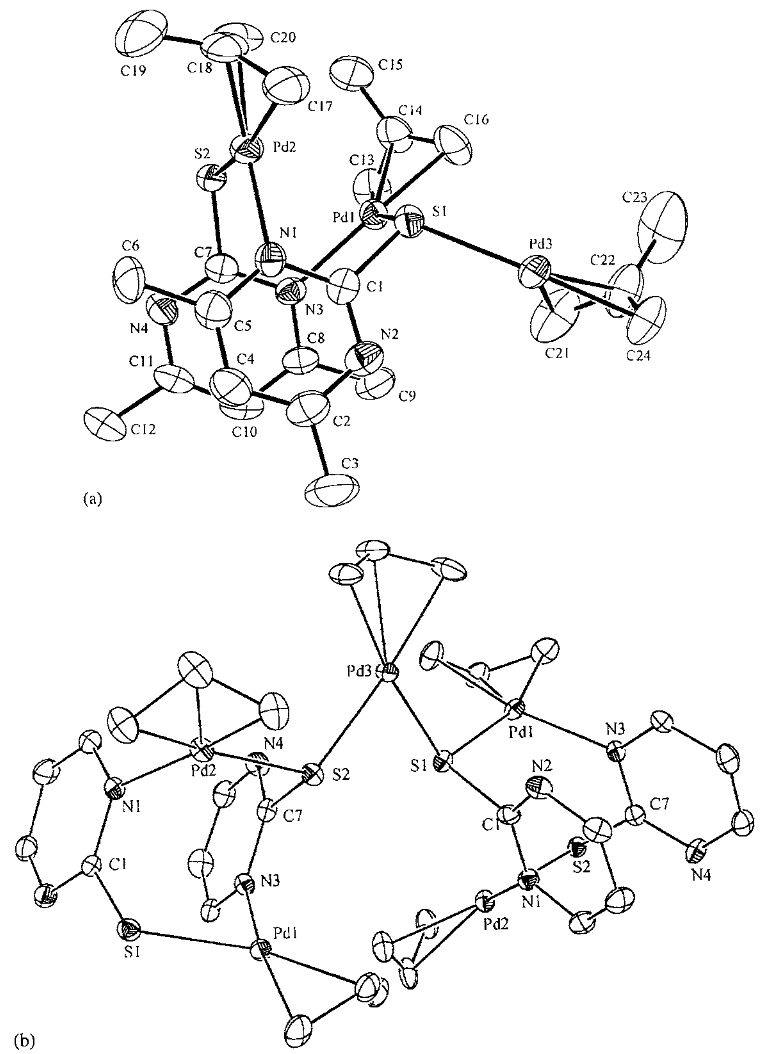


Fig. 2. (a) ORTEP drawing (50% probability level) of trimetallic cationic fragment in the asymmetric unit of the structure of **5**. (b) A partial view of an infinite chain showing the connection of two discrete trimetallic units. Selected interatomic distances (Å) and angles (°): Pd1···Pd2 3.616(1), Pd1···Pd3 4.038(1), Pd2···Pd3 5.492(1), Pd2···Pd3* 4.160(1), Pd1–S1 2.375(2), Pd1–N3 2.136(6), Pd2–S2 2.385(2), Pd2–N1 2.128(6), Pd3–S1 2.387(2), Pd3–S2* 2.368(2), S1–Pd1–N3 96.5(2), S2–Pd2–N1 96.7(2), S1–Pd3–S2* 90.7(1), S1–C1–N1 115.6(6), S2–C7–N3 115.6(5). Pd–C (allyl) bond lengths fall in the range 2.095(9)–2.151(9) Å.

*3.3. Synthesis of complex **3***

Complex **3** was obtained by a similar method as described for **2**, using [K{im(Me)S}] (0.100 g, 0.650 mmol) and an equimolecular amount of [Pd(η^3-C_4H_7)](CF_3SO_3). Yield: 0.153 g. (85%). Anal. Found: C, 34.78; H, 4.51; N, 9.76%. $C_8H_{12}N_2PdS$. Calc.: C, 34.98; H, 4.40; N, 10.20%.

*3.4. Synthesis of complex **4***

Complex **4** was obtained by a similar method as described for **2**, using [Kpm(Me)$_2$S)}] (0.100 g, 0.560 mmol) and an equimolecular amount of [Pd(η^3-C_4H_7)](CF_3SO_3) (0.174 g, 0.560 mmol). Yield: 0.123 g. (73%). Anal. Found: C, 39.94; H, 4.79; N, 8.74%. $C_{10}H_{11}N_2PdS$. Calc.: C, 39.96; H, 4.65; N, 9.32%.

*3.5. Synthesis of complexes **5***

A CH_2Cl_2 solution of **4** (0.200 g, 0.221 mmol) was treated with KCF_3SO_3 (0.041 g, 0.221 mmol). After 2 days of stirring at room temperature, the solution was concentrated and a crystalline orange solid was formed. The solvent was filtered off and the crystals, which corresponds to complex **5**, were isolated. ^{19}F-NMR $(CD_3)_2CO$: δ −79.96 (s, CF_3SO_3). Yield: 0.127 g. (63%). Anal. Found: C, 33.12; H, 4.07; N, 6.46%. $C_{25}H_{35}F_3N_4Pd_3O_3S_3$. Calc.: C, 32.97; H, 3.88; N, 6.16%.

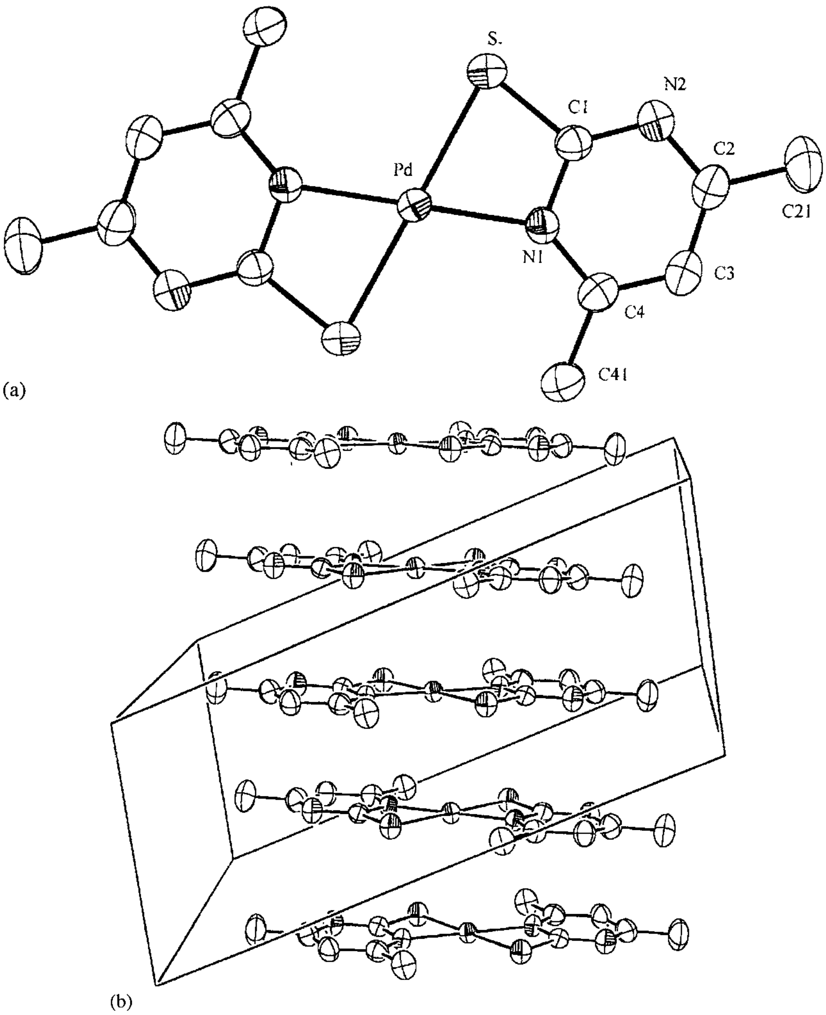


Fig. 3. (a) ORTEP drawing (50% probability level) of the molecule in **6**. (b) packing of monomeric molecules down the *z*-direction, one chain is shown. Selected interatomic distances (Å) and angles (°): Pd···Pd 3.519(1), Pd–S 2.341(1), Pd–N1 2.016(3), S–Pd–N1 70.2(1), S–Pd–N1* 109.8(1), S–C1–N1 108.7(3).

3.6. Synthesis of complexes ***6***

When a CH_2Cl_2 solution of **5** (0.200 g, 0.219 mmol) was kept at room temperature for 2 weeks, yellow crystals of **6** were obtained after concentration and filtration of the resulting suspension. Anal. Found: C, 37.65; H, 3.88; N, 14.91%. $C_{12}H_{14}N_4PdS_2$. Calc.: C, 37.46; H, 3.64; N, 14.57%. Yield: 0.093 g (37%).

3.7. X-ray structure analyses of complexes ***5*** *and* ***6***

Crystals suitable for X-ray diffraction studies were grown from dichloromethane/diethyl ether solutions. All measurements have been carried out on an Enraf–Nonius CAD4 diffractometer at room temperature. The unit cells were determined for each crystal from 25 reflections selected by CAD4 routines. Data reductions were performed with MolEN package [11]. Intensities were corrected for Lorentz and polarization effects as well as for linear decay. The Ψ-scan empirical absorption corrections were applied for both sets of reduced data.

The structures were solved and refined by conventional Patterson, difference Fourier, and full-matrix least-squares methods by using squared structure amplitudes (F^2) for calculations with SHELXL97 program [12]. The CF_3 fragment of the anion in the structure of **5** is disordered and was refined giving 0.5 occupancies for fluorine atoms. The hydrogen atoms were placed in calculated positions and included in the final cycles of refinements in a riding model. The pertinent crystallographic data are gathered in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic

Table 3
Crystallographic data for **5** and **6**

	5	**6**
Formula	$C_{25}H_{37}F_3N_4O_4Pd_3S_3$	$C_{12}H_{14}N_4PdS_2$
Color	Yellow	Yellow
Dimensions (mm)	0.4 × 0.2 × 0.08	0.25 × 0.1 × 0.05
Formula weight (g)	929.97	384.79
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
Cell dimensions:		
a (Å)	10.945(1)	15.922(1)
b (Å)	13.788(2)	13.149(2)
c (Å)	22.261(4)	7.038(1)
β (°)	91.292(1)	104.98(1)
V (Å^3)	3358.6(8)	1423.4(3)
Z	4	4
ρ_{calc}, (g cm^{-3})	1.839	1.796
F(000)	1840	768
Linear abs. μ (cm^{-1})	18.28	15.88
Radiation (Å) λ(Mo–K_α)	0.71073	0.71073
Temperature (K)	293(2)	293(2)
Scan type	ω	ω
Scan speed (° min^{-1})	1.4–16.6	1.4–16.6
Scan width (°)	$\omega = 0.78 + 0.347 \tan \theta$	
θ range (°)	2.35–26.29	2.65–26.30
Decay (%)	−1.4, Corrected	−0.9, Corrected
Abs. corr. (Ψ scan)	72.30–99.98	90.86–99.86
Cut off for obsd. data	$I > 2\sigma(I)$	$I > 2\sigma(I)$
Unique obsd. data (NO)	4645	949
No. of variables (NV)	381	95
R_1, on F^2	0.046	0.028
wR_2, on F^2	0.123	0.064
GOF	1.055	1.044
ρ_{max}, ρ_{min} (e Å^{-3})	+3.01[a], −1.55[a]	+0.50, −0.44

[a] In F_3CSO_3 disordered anion.

Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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