



[Pd{2-CH₂-5-MeC₆H₃C(H)=NN=C(S)NHet}]₃: An unprecedented trinuclear cyclometallated palladium(II) cluster through induced flexibility in the metallated ring

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ABSTRACT

The reaction of 1-(2,5-dimethylbenzylidene)-3-ethylthiosemicarbazone and palladium acetate in acetic acid yields a trinuclear cyclometallated palladium(II) compound. Each thiosemicarbazone ligand is tridentate with the metal bonded to the carbon atom from the 2-methyl group, to the azomethine nitrogen and to the sulfur atom, which bridges to an adjacent palladium center. The crystal structure confirms the presence of a non-planar hexagonal metallated ring plus a central six-membered palladium–sulfur core within the trimer, which also displays a rather deep intramolecular cavity.

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1. Introduction

The cyclometallation reaction has been profusely investigated in view of the rich chemistry it renders and is well documented for a great variety of metal centers and ligands [1]. The ensuing compounds are successfully used in organic synthesis [2], catalysis [3], photochemistry [4] and optical resolution process [5], and are rather promising as potential biologically active materials [6] and liquid crystals [7]. Among the numerous ligands prone to undergo metallation, thiosemicarbazones in particular, are most interesting because they are readily metallated by Ru(II) [8], Rh(III) [9], Pd(II) [10] and Pt(II) [11] with activation of a C–H bond. Palladium(II) salts, such as palladium(II) acetate or potassium tetrachloropalladate(II) give tetranuclear species with a Pd₄S₄ core [10,12]. Furthermore, the previous studies by us and others related to thiosemicarbazone palladacycles and platinacycles have shown that tetrameric species are obtained in all cases with two pairs of parallel metallated units set mutually at ca. 90° [10,12] (Fig. 1). Even in the absence of metal–carbon bond, with the metal only bonded to the nitrogen and sulfur atoms, the tetrameric nature of the structure persists [13]. The ability shown by these ligands to produce such compounds is due, in part, to the bonding properties of the sulfur atom in its thiolate form which enables it to bind two metal atoms in a chelating and bridging mode simultaneously.

We have also found [10,14] that the strength of the palladium–sulfur bond, following Pearson's concept [15], allows the ligand to be tightly bonded to the metal as terdentate [C,N,S] clamping firmly three of the metal coordination positions, preventing reaction of the Pd–N bond situated in the central part of the two fused five-membered rings at the metal center; upon reaction with diphosphines with small bite angles the new cyclometallated bidentate P,S metaloligands have been obtained [16]. Therefore, having previously studied the tetranuclear thiosemicarbazone species our perspectives for the advancement into further aspects related to the chemistry of these compounds was to seek new structural features induced by alterations in the nature of the ligand and of its reactivity towards the palladium substrate; the alternative thus being modifications in the central palladium/sulfur ring. We reasoned that altering the size and the flexibility of the five-membered cyclometallated ring, [Pd–C=C=N], should change the angle between the palladium coordination plane and the metallated phenyl ring, as well as modifying the angles between the palladium coordination planes themselves, thus hindering formation of the tetrameric structure and bringing about alterations in the number of atoms and in the geometry of the Pd_nS_n core. In order to achieve this, Pd–C bond formation should arise at a carbon atom other than a phenyl ring, as for example, a methyl aliphatic carbon atom. For the study we sought out the ligand 2,5-Me₂C₆H₃C(H)=NN(H)C(=S)NHet and attempted to metallate the methyl group to give the more flexible six-membered cyclometallated ring, in the hope that the steric requirements of the 5-Me

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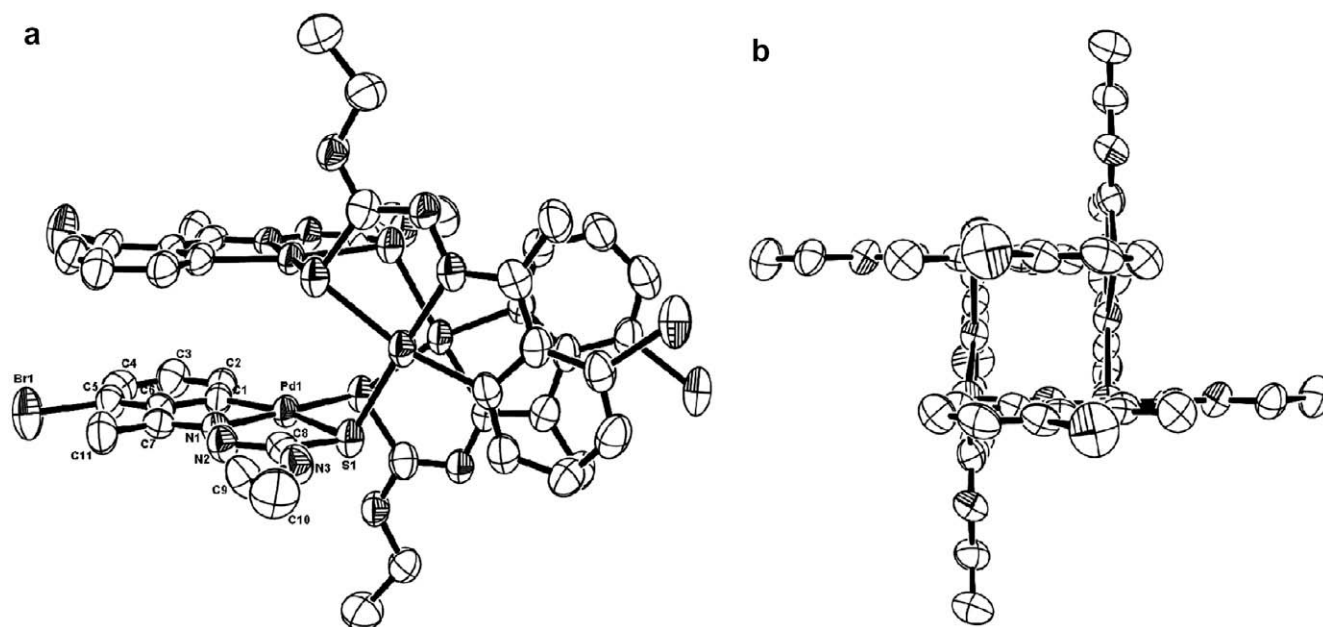


Fig. 1. (a) Tetranuclear structure of a cyclometallated palladium(II) compound with a terdentate [C,N,S] thiosemicarbazone. (b) View along the *c* axis showing the S_4 -symmetry.

group would sufficiently hinder metallation of the C6 atom. Palladacycles bearing metallated sp^3 carbon atoms are known with, e.g., phosphorus donor ligands [17], methylquinoline [18]; and metallation of methyl groups attached to phenyl rings rendering six-membered metallacycles is scarce and limited to Schiff base ligands where methyl substituents occupy the two possible metallation sites [19]. Furthermore, although several examples of trinuclear cyclometallated palladium(II) compounds are known, such as Steels compound [20], and also trimers that display structures which may be described crudely as an equilateral triangle with the palladium atom at each vertex [21], the present investigation brings about an altogether different structure with the metal and the sulfur donor atoms linked together in a crown-type nucleus. What follows are our findings in the synthesis, structure and characterization of a new type of trinuclear palladacycle.

2. Experimental

2.1. General comments

Solvents were purified by standard methods [22]. Chemicals were used as supplied from commercial sources. Elemental analyses were carried out by the Unidate de Analise Elemental de la Universidad de Santiago de Compostela using a Carlo-Erba elemental analyzer, Model 1108. IR spectra were recorded as Nujol mulls or polythene discs on Perkin–Elmer 1330, Mattson Model Cygnus-100 and Bruker Model IFS-66V spectrophotometers. NMR spectra were obtained as $CDCl_3$ solutions and referenced to $SiMe_4$, and were recorded on a Bruker AMX 300 spectrometer. All chemical shifts are reported downfield from standards. The FAB mass spectra were recorded with a Fisons Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix.

2.2. 2,5- $Me_2C_6H_3C(H)=NN(H)C(=S)NHET$ (**1**)

To a suspension of the thiosemicarbazide (500 mg, 4.2 mmol) in water (40 cm^3) 35% hydrochloric acid (0.6 cm^3) was added to give a clear solution. Then 2,5-dimethylbenzaldehyde (563 mg, 4.2 mmol) was added and the resulting mixture was stirred at room tempera-

ture for 4 h. The solid formed was filtered off, washed with cold water and dried *in vacuo*.

Yield: 957 mg, 97%. Anal. Found: C, 61.3; H, 7.3; N, 17.9; S, 13.5%; $C_{12}H_{17}N_3S$ (235.35) requires C, 61.2; H, 7.3; N, 17.8; S, 13.6. IR: $\nu(N-H)$ 3412s, 3153s cm^{-1} ; $\nu(C=N)$ 1586s, br cm^{-1} ; $\nu(C=S)$ 806m cm^{-1} . 1H NMR ($CDCl_3$, δ ppm, *J* Hz): 1.31 (t, 3H, $NHCH_2CH_3$, $^3J(HH) = 7.3$); 2.34, 2.40 (2s, 6H, Me); 3.76 (qd, 2H, $NHCH_2CH_3$, $^3J(HH) = 7.3$, $^3J(NHCH_2) = 4.9$); 7.08 (b, 2H, H3 y H4); 7.42 (s, 1H, $NHCH_2CH_3$); 7.54 (s, 1H, H6); 8.23 (s, 1H, $HC=N$); 10.31 (s, 1H, NH).

2.3. $[Pd\{2-CH_2-5-MeC_6H_3C(H)=NN=C(S)NHET\}]_3$ (**2**)

The ligand **1** (235 mg, 1.0 mmol) and palladium(II) acetate (213 mg, 0.95 mmol) were added to 40 cm^3 of acetic acid to give a clear solution, which was stirred at 60 °C for 8 h. After cooling to room temperature the solution obtained was filtered through celite to remove the black palladium formed, the solvent removed and the residue extracted with dichloromethane. The combined extracts were dried overnight with anhydrous magnesium sulphate, and chromatographed on a column packed with silica gel. Elution with dichloromethane afforded the final product as an orange solid after concentration. Yield 290 mg 90%. Anal. Found: C, 42.4, H, 4.4, N, 12.4, S, 9.3%. $C_{36}H_{45}N_9S_3Pd_3$ (1019.21) requires C, 42.4, H, 4.5, N, 12.4, S, 9.4. IR: $\nu(C=N)$ 1565m, cm^{-1} . 1H NMR ($CDCl_3$, δ ppm, *J* Hz): 1.29 (t, 2H, CH_2CH_3); 2.23 (s, 3H, Me); 3.10 (s, 2H, CH_2); 3.47 (m, 2H, CH_2CH_3); 4.99 (m, 1H, $NHET$); 6.89 (s, 1H, H6); 6.93 (d, 1H, H4); 7.10 (d, 1H, H3, $^3J(H3H4) = 7.9$); 7.91 (s, 1H, $HC=N$). FAB-MS: m/z 1019 $[M]^+$.

2.4. Crystal structure of **2**

For **2** room temperature X-ray data were collected on a BRUKER SMART-CCD-1000 diffractometer using monochromated $Mo\ K\alpha$ radiation by the omega method. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semiempirical methods (SADABS) based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least-squares on F^2 . Hydrogen

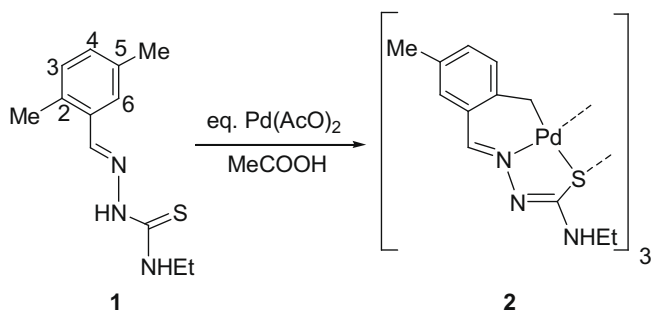
atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0454$ and $wR_2 = 0.0829$ (all unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms, except C(23), C(24), C(35) and C(36). The structure solutions and refinements were carried out with the SHELX-97 program package [23].

3. Results and discussion

The neutral complex, $[\text{Pd}\{2\text{-CH}_2\text{-5-MeC}_6\text{H}_3\text{C(H)=NN=C(S)NHEt}\}_3]$ (**2**), is homoleptic presenting one thiosemicarbazone unit for each palladium atom. This compound was made from the reaction of 2,5-Me₂C₆H₃C(H)=NN(H)C(=S)NH₂ and Pd(O₂CMe)₂ in 90% yield after recrystallization (Scheme 1). Compound **2** was unambiguously analyzed by CHN and mass spectrometry and further characterized by ¹H NMR spectroscopy. In the trimer each thiosemicarbazone ligand is terdentate [C,N,S] with the metal bonded to the 2-methyl group, to the azomethine nitrogen and to the sulfur atom, which bridges to an adjacent palladium center; the fourth coordination site of the metal is occupied by a sulfur from a neighboring metallated unit. The mass spectrum (FAB) showed a peak at m/z 1019 for the molecular ion whose isotopic composition is in agreement with a trinuclear complex of formula C₃₆H₄₅N₉Pd₃S₃, and there is no evidence of tetramers or higher order aggregates. The main features in the IR spectrum are: absence of the $\nu(\text{N-H})$ and $\nu(\text{C=S})$ stretches, the latter in accordance with loss of the double-bond character upon deprotonation of the NH group, which is reflected in the lengthening of the C–S bond in the structure (*vide infra*); shift of the $\nu(\text{C=N})$ band to lower wavenumbers upon complex formation [25]. The ¹H NMR spectrum is indicative of a C₃-symmetry species in solution with only one set of signals being observed. The data are in agreement with the presence of only one methyl group and of the expected methylene group, consequent upon metallation, *per* monomeric unit, with a singlet at δ 2.23 (3H, Me) and a doublet of doublets at δ 3.10 (2H, CH₂) for the non-equivalent methylene protons. Three aromatic proton signals at δ 6.89s (H6), δ 6.93d (H4) and δ 7.10d (H3), evidences non-metallation of the phenyl ring carbon atoms. The absence of the signal for the NH group in the ¹H NMR spectrum reveals deprotonation as observed in coordination compounds of these ligands [24], and the HC=N signal is upfield shifted consequent upon Pd–N bond formation [12b].

3.1. Crystal structure of complex 2

Crystals of **2** were obtained by slow evaporation from a chloroform solution, space group $P2(1)/c$, with four independent molecules in the asymmetric unit. Crystal data are shown in Table 1 and ORTEP views of the structure are depicted in Figs. 2 and 3. The result from the X-ray crystallographic study on **2** confirms the NMR data.



Scheme 1. Formation of the trinuclear cyclometallated Pd(II) cluster **2**.

Table 1

Crystal data and structure refinement data for **2**.

Empirical formula	C ₃₆ H ₄₅ N ₉ Pd ₃ S ₃
Formula weight	1019.19
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	
<i>a</i> (Å)	10.562(5)
<i>b</i> (Å)	20.083(5)
<i>c</i> (Å)	19.459(5)
β (°)	100.721(5)
Volume (Å ³)	4056(2)
<i>Z</i>	4
D_{calc} (Mg/m ³)	1.649
Absorption coefficient (mm ⁻¹)	1.508
$F(000)$	2040
Crystal size (mm ³)	0.30 × 0.9 × 0.05
θ Range for data collection (°)	1.47–21.97
Index ranges	–11 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 21, 0 ≤ <i>l</i> ≤ 20
Reflections collected	23 710
Independent reflections	4953 [$R_{\text{int}} = 0.0915$]
Completeness to $\theta = 21.97^\circ$	100.0%
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4953/0/450
Goodness-of-fit on F^2	1.096
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0454$, $wR_2 = 0.0829$
<i>R</i> indices (all data)	$R_1 = 0.1186$, $wR_2 = 0.1171$
Largest difference in peak and hole (e Å ⁻³)	0.614 and –0.732

Fig. 2 reveals that the highly symmetric Pd₃S₃ core consists of a six-membered ring of alternating palladium and sulfur atoms, which may be viewed as two staggered Pd₃ and S₃ quasi parallel triangles at 175.45(0.06)°.

The remaining two sites of each square-planar palladium coordination sphere are occupied by the alkyl carbon atom from the methylene group and the nitrogen atom of the C=N unit. As with the Pd₄S₄ complexes, this structure depicts the bonding inherent to thiosemicarbazone palladacycles where each sulfur atom within the metallacycle bridges to another palladium atom. Each of the three palladium atoms belongs to two fused six and five-membered chelate rings: the C,N metallacycle and the N,S-chelate moiety, respectively, as a result of bonding to a tridentate C,N,S ligand (Fig. 2). The angles between adjoining atoms in the coordination sphere of each metal atom are close to the theoretical value of 90°; with the most noteworthy strains in the N–Pd–S values, *ca.* 82°, due to formation of the N,S chelate ring. The Pd–C bond distances [2.038(11)–2.058(11) Å] are shorter than the expected value of 2.081 Å [26], but nevertheless somewhat longer than those found earlier in related tetranuclear palladium structures [*cf.* 2.021(5) Å [12b], 1.999(9)–2.016(9) Å [10], 1.990(7) Å [12a]. The C–S [1.775(13)–1.804(12) Å] and the C–N_{hydrazynic} [1.276(14)–1.300(15) Å] bond distances are consistent with increased single-bond and double-bond character, respectively, in the deprotonated form. The Pd–S_{bridging} bond lengths [2.316(13)–2.322(4) Å], *trans* to nitrogen, are shorter than the Pd–S_{chelating} bonds [2.383(3)–2.421(3) Å], *trans* to carbon, reflecting the differing *trans* influence of the methylene carbon and nitrogen atoms of the coordinated ligand. Contrary to a recent example where the metallated ring is essentially planar [12b], herein the metallated rings are puckered with the palladium atoms deviating from the mean planes defined by the carbon and nitrogen atoms by 0.882–1.064 Å. The Cremer and Pople puckering parameters [27] are in accordance with a conformation midway between half-boat and twist-boat [$Q = 0.598(13)$ – $0.730(12)$, $\theta = 115.6(13)$ – $118.2(13)$, $\varphi = 146.9(16)$ – $149.0(12)$]; *cf.* with the values for the Pd₃S₃ ring with a chair conformation [$Q = 1.546(3)$, $\theta = 5.07(11)$, $\varphi = 280.1(12)$]. The palladium coordination planes at Pd(1), Pd(2) and Pd(3) are essentially planar,

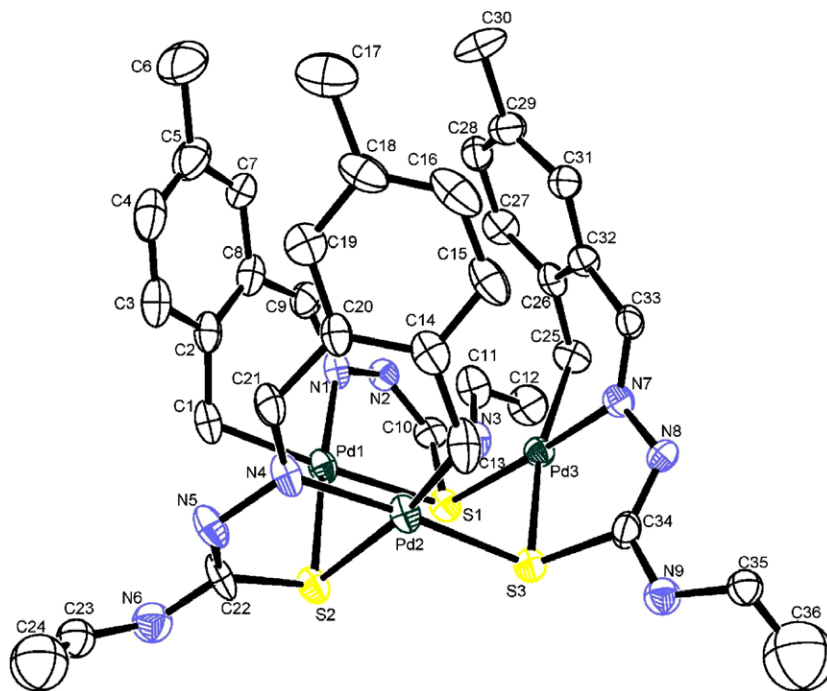


Fig. 2. The monomeric cyclometallated unit showing bonding of the tridentate [C,N,S] thiosemicarbazone.

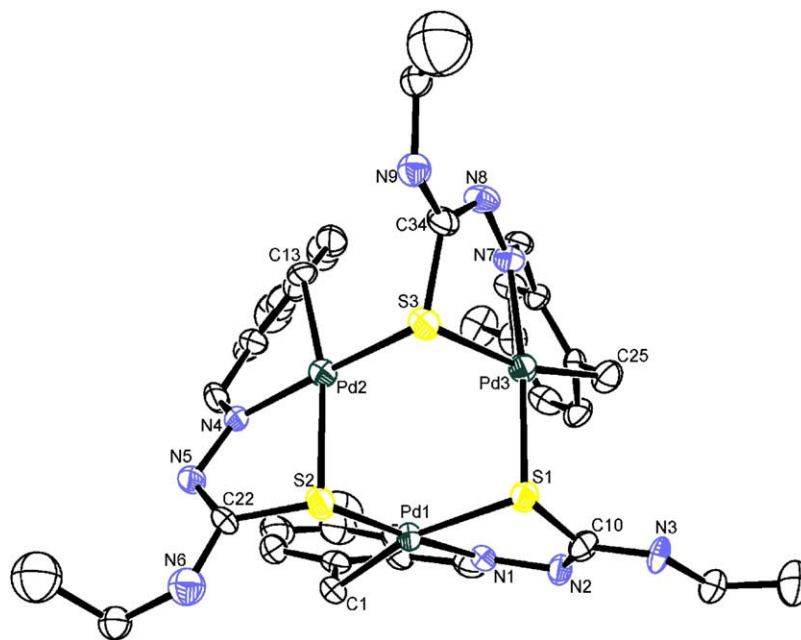


Fig. 3. Molecular structure of (2) $[\text{Pd}(2\text{-CH}_2\text{-5-MeC}_6\text{H}_3\text{C(H)=NN=C(S)NHet})]_3$. Thermal ellipsoids drawings are shown at the 30% probability level. Selected bond lengths and angles: Pd(1)–C(1) 2.038(11); Pd(1)–N(1) 2.001(11); Pd(1)–S(1) 2.403(3); Pd(1)–S(2) 2.322(4); S(1)–C(10) 1.782(13); N(1)–C(9) 1.216(13); N(2)–C(10) 1.299(14); Pd(2)–C(13) 2.053(11); Pd(2)–N(4) 2.025(10); Pd(2)–S(2) 2.421(3); Pd(2)–S(3) 2.316(3); S(2)–C(22) 1.775(13); N(4)–C(21) 1.270(14); N(5)–C(22) 1.300(15) Å. Pd(3)–C(25) 2.038(12); Pd(3)–N(7) 2.051(9); Pd(3)–S(1) 2.316(3); Pd(3)–S(3) 2.383(3); S(3)–C(34) 1.804(12); N(7)–C(33) 1.286(14); N(8)–C(34) 1.276(14) Å. N(1)–Pd(1)–C(1) 86.4(5); N(1)–Pd(1)–S(2) 176.5(3); C(1)–Pd(1)–S(2) 96.2(4); N(1)–Pd(1)–S(1) 82.7(3); C(1)–Pd(1)–S(1) 165.9(4); S(2)–Pd(1)–S(1) 94.97(12); N(4)–Pd(2)–C(13) 86.3(4); N(4)–Pd(2)–S(3) 175.8(3); C(13)–Pd(2)–S(3) 97.3(4); N(4)–Pd(2)–S(2) 81.7(3); C(13)–Pd(2)–S(2) 167.6(3); S(3)–Pd(2)–S(2) 94.64(11); C(25)–Pd(3)–N(7) 85.3(4); C(25)–Pd(3)–S(1) 98.2(4); N(7)–Pd(3)–S(1) 173.8(3); C(25)–Pd(3)–S(3) 166.3(4); N(7)–Pd(3)–S(3) 82.3(3); S(1)–Pd(3)–S(3) 94.70(11).

with rms values of 0.0981, 0.0238 and -0.0881 , respectively, with angles between planes from $81.41(10)^\circ$ to $87.56(10)^\circ$, as opposed to the parallel/perpendicular arrangement in the tetranuclear moieties. The intramolecular Pd...Pd distances range from $3.281(3)$ to $3.565(3)$ Å. There are no noteworthy intermolecular hydrogen-bonding contacts.

Fig. 3 shows a second view of 2, namely along the axis perpendicular to the plane formed by the three palladium atoms; showing

the six-membered Pd_3S_3 ring and the approximate C_3 -symmetry in the solid state [cf. S_4 -symmetry in Fig. 1b]. This perspective shows a rather deep intramolecular cavity enclosed within the three metallated rings and the three phenyl rings. The distance from the S(1)–S(2)–S(3) plane to the C(5)–C(18)–C(19) plane is 6.626 Å (Fig. 4). The cavity is somewhat narrower at the phenyl end, with distances between the ring centers estimated from 4.849 to 5.379 Å, and angles between planes from 55.78° to 66.16° .

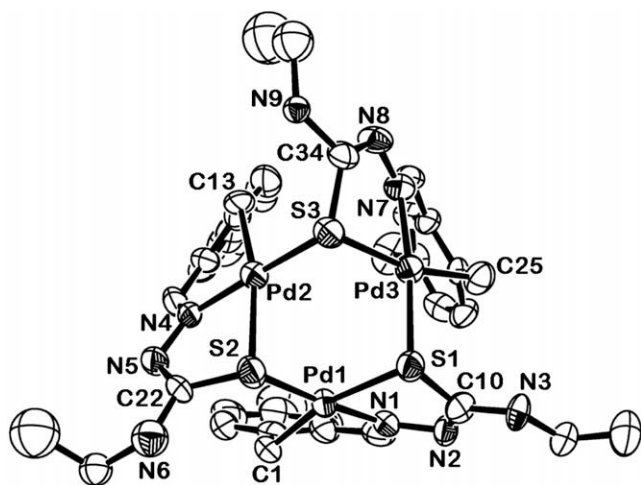


Fig. 4. View along the axis perpendicular to the least-square plane of the Pd₃S₃ ring.

4. Conclusions

We have produced the first example of a trinuclear homoleptic thiosemicarbazone palladacycle by metallation of the ligand at an aliphatic carbon atom, which has been fully characterized both in solution and in the solid state. Thus, palladacycles derived from thiosemicarbazones that behave as [CNS] pincer-type ligands, are not only capable of yielding tetranuclear compounds bearing a Pd₄S₄ core, but properly designed as in the present case, may generate a new class of palladacycles featuring both the less commonly encountered metallation of a sp³ aliphatic carbon atom and a central ring six-membered Pd₃S₃ ring as well, as opposed to the few known triangular trimer species [21] and to Steels compound [20].

5. Supplementary material

CCDC 278846 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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