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Preparation, Structure and Spectroscopic Studies of the Palladium Mercaptides $Pd_8(S\text{-}nPr)_{16}$ and $Pd_6(S\text{-}nPr)_{12}$

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Abstract

Various palladium salts react with n-propane thiol to form a mixture of the cyclic mercaptides $Pd_8(S\text{-}nPr)_{16}$ (**I**) and the known $Pd_6(S\text{-}nPr)_{12}$ (**II**). **I** is described as an octagonal toroid, containing a planar ring of palladium atoms, each being bridged by four mercapto groups in approximately square planar geometry. The pendant n-propyl groups radiate outward in approximately axial and equatorial orientations with respect to the ring, which was also observed in solution by ^1H and ^{13}C NMR. Crystal data: space group $C2/c$, $a = 22.251(15)$, $b = 27.623(6)$, $c = 14.621(17)$ Å, $\beta = 116.35°(4)$, $V = 8053(4)$ Å^3. Least-squares refinement based on 3103 observed reflections led to an R value of 0.078. **I** and **II** failed to complex any appropriate guest species, as evidenced by the UV–Vis spectra. **I** was found to have a reversible oxidation wave at $E/2 = 0.77$ V, and a irreversible oxidation wave of 1.09 V. **II** displayed two irreversible peak potentials at 0.77 and 1.09 V. In each case, the waves were one electron processes, in which the reversibility was not enhanced at low temperatures.

Introduction

The mercapto group has been shown to act as a bridge between various metal atoms, forming complexes of the general structure $M_n(SR)_{2n}$ [1]. R groups such as ethyl and phenyl form insoluble complexes with the platinum group metals, and their respective structures were proposed accordingly as being polymeric in nature [2]. More recently, it has been found that the analogous complexes derived from thiols with more solubilizing R groups can be readily crystallized. X-ray diffraction analyses have revealed the formation of symmetrical molecular cycles, such as $Ni_4(SR)_8$ [3], $Pd_6(SR)_{12}$ [4], and $Ni_8(SR)_{16}$ [5]. These 'tiara' like structures are composed of nearly planar rings of metal atoms, each square planar metal being bridged by four mercapto ligands. The pendant chains from each sulfur atom alternate in approximately equatorial and axial orientations in relation to the plane of the ring.

Because of their ring-like structures, these mercaptide complexes have been proposed as potential macromolecular inclusion hosts [6], perhaps inorganic analogs of cyclodextrins. Much of their chemistry and spectroscopic properties, however, have remained uninvestigated. Here we report the preparation, structure and chemistry of the new $Pd_8(S\text{-}nPr)_{16}$ octagonal toroid (**I**). The NMR, UV–Vis, and electrochemical behavior of **I** and its hexagonal homolog $Pd_6(S\text{-}nPr)_{12}$ [4] (**II**) were also investigated.

Experimental

Preparation of Palladium n-Propyl Mercaptides I and II

100 mg of Li_2PdCl_4 (0.382 mmol) was dissolved in 5 ml methanol, and 58 mg of n-propane thiol (0.764 mmol) in 5 ml methanol was added dropwise. An orange precipitate formed immediately, and the mixture was stirred at 70 °C for 4 h whereupon most of the solid went into solution. *ca.* 20 ml CH_2Cl_2 was added, and the solution was washed with one 20 ml portion of 10% NaOH. After drying over $MgSO_4$, the solvent was evaporated, leaving an amorphous orange solid, 0.78 g, quantitative. ^1H NMR (400 MHz, $CDCl_3$); m, 2.42 (4H), m, 1.80 (4H), m, 1.10 (6H); IR (CCl_4), 2900 cm^{-1}. The amorphous solid was dissolved in pyridine, and allowed to stand at 25 °C for 2 days, after which two types of crystals cocrystallized. The first were light orange prisms (**I**) melting point (m.p.) = 154 °C, and the others (formed in a slightly larger amount) were dark orange cubes (**II**) m.p. = 273 °C. ^1H NMR (400 MHz, $CDCl_3$): **I**, t, 2.45 (2H 7Hz), t, 2.39 (2H 8Hz), m, 1.90 (4H), t, 1.13 (3H 7Hz), t, 1.07 (3H 8Hz); **II**, m, 2.40 (4H), m, 1.82 (2H 8Hz), m, 1.78 (2H 8Hz), t, 1.67 (3H 7Hz), t, 1.06 (3H 7Hz). ^{13}C NMR (400 MHz, $CDCl_3$): **I**, 36.96, 31.31,

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TABLE I. Crystallographic Data for $Pd_8(S\text{-}nPr)_{16}$ (I)

Molecular formula	$C_{48}H_{112}S_{16}Pd_8$
Crystal system	monoclinic *c*
Cell dimensions	$a = 22.251(15)$ Å $\beta = 116.35(4)°$ $b = 27.623(6)$ Å $\alpha = \gamma = 90.00°$ $c = 14.621(17)$ Å $V = 8053$ Å^3
Wavelength	0.71069 Å (Mo Kα)
Range of 2θ	3.5°–45°
Space group	*C2/c*
Z	4
Calculated density	1.84 g/cm^3
Linear absorption coefficient	21.60 cm^{-1}
Number of unique reflections	3103
Structure factor weights	$w = 1/[\sigma^2(F) + 0.0008F^2]$ with $\sigma^2(F)$ from counting statistics
Final *R* factors	$R = 0.078$ $R_w = 0.078$
Goodness of fit (nominal)	1.620
Goodness of fit (divided by slope of normal probability plot)	1.157
Crystal dimensions (mm)	0.05 × 0.1 × 0.4

28.13, 27.56, 14.05, 13.78; **II**, 36.65, 32.32, 28.42, 25.95, 13.67, 13.27. Satisfactory C and H elemental analyses were obtained for **I** and **II**.

Crystallography

Diffraction data collected on a Nicolet R3m/E diffractometer revealed that complex **I** crystallized in the monoclinic *c* lattice type, and examination of the systematic absences suggested the *C2/c* space group. After calculation of an empirical absorption correction, the structure was solved using the SHELXTL program system, in which the palladium atoms were located using Patterson methods. The positions of the lighter atoms were subsequently discerned from Fourier difference maps. All non-hydrogen atoms were refined with anisotropic thermal parameters, and two of the propyl groups, which were associated with the palladiums near the *C2* axis were found to be partially disordered. The hydrogen atoms were inserted at their appropriate theoretical positions. Pertinent crystallographic data for **I** are given in Table I, and the atomic coordinates are tabulated in Table II. See also 'Supplementary material'.

TABLE II. Atomic Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for I

Atom	*x*	*y*	*z*	U^a
Pd(1)	3766(1)	3231(1)	675(1)	102(1)*
Pd(2)	4148(1)	1275(1)	1244(1)	91(1)*
Pd(3)	4162(1)	5146(1)	1255(1)	101(1)*
Pd(4)	5000	549(1)	2500	91(1)*
Pd(5)	5000	5867(1)	2500	89(1)*
S(1)	3871(2)	570(3)	1871(2)	104(3)*
S(2)	3130(2)	4413(3)	780(2)	103(2)*
S(3)	4457(2)	2056(3)	657(2)	112(3)*
S(4)	4387(2)	4448(3)	597(2)	112(3)*
S(5)	5159(2)	520(3)	1724(2)	115(3)*
S(6)	3892(2)	5904(4)	1871(2)	133(3)*
S(7)	3138(2)	2005(3)	724(2)	105(3)*
S(8)	5202(2)	5871(4)	1744(2)	139(3)*
C(1)	2707(7)	2250(11)	1130(6)	118(6)
C(2)	2168(8)	1542(11)	1031(6)	144(7)
C(3)	4986(9)	7111(10)	1503(4)	146(7)
C(4)	3990(8)	1550(7)	−12(6)	153(7)
C(5)	2772(8)	5034(6)	142(6)	126(6)
C(6)	3666(10)	−609(10)	1621(8)	162(8)
C(7)	5280(7)	4159(12)	896(7)	134(6)
C(8)	1883(12)	1720(15)	1428(8)	211(11)
C(9)	3378(11)	5212(16)	2098(9)	184(9)
C(10)	4231(11)	601(9)	−30(10)	207(11)
C(11)	5433(10)	3869(15)	442(8)	177(9)
C(12)	3895(17)	450(23)	−637(11)	328(19)
C(13)	4837(14)	7118(19)	921(5)	239(13)
C(14)	2605(11)	6035(8)	108(9)	185(9)
C(15)	5860(9)	1325(14)	1830(8)	157(8)
C(16)	6174(11)	3675(18)	654(10)	241(13)
C(17)	4653(17)	8099(19)	814(13)	306(18)
C(18)	3761(16)	−1337(20)	2033(12)	280(15)
C(19)	2243(14)	6228(19)	436(11)	267(14)
C(20)	5699(20)	2228(20)	2008(15)	187(13)
C(21)	6299(27)	2838(41)	2136(28)	292(21)
C(22)	3682(18)	4276(19)	2253(16)	174(12)
C(23)	4268(23)	3629(36)	2488(24)	363(26)
C(24)	3173(19)	−1319(30)	2149(17)	399(25)
C(21a)	7023(28)	1388(42)	1852(23)	292(21)
C(20a)	6446(21)	819(35)	1829(23)	187(13)
C(22a)	2870(22)	5885(31)	2104(22)	174(12)
C(23a)	2572(45)	5078(51)	2256(39)	363(26)

^{a}Starred items: equivalent isotropic *U* defined as one third of the trace of the orthogonalised *U* tensor.

UV–Vis Absorption Studies on I and II

Solutions of **I** and **II** in hexane in the order of 0.2 mM were prepared, and their UV–Vis spectra were determined on a Perkin-Elmer 552A spectrophotometer at room temperature. Absorption maxima: **I**, 395 nm ($\epsilon = 4400$), 330 (9600), 265 (12 000), 230 (7200); **II**, 410 nm (4500), 305 (10 000), 265 (16 000).

Electrochemistry

Electrochemical experiments on **I** and **II** were carried out at 25, 0, −40, and −60 °C in N_2 purged reagent grade CH_2Cl_2 containing 0.1 M $(NBu)_4PF_6$ as the supporting electrolyte. The cyclic voltammograms were recorded on a BAS CV27 potentiostat using 200 mV/s scan rates. A glassy carbon electrode was used as the working electrode, and all potentials were measured against a Ag/AgCl reference electrode. The peak and half wave potentials are reported (*vide infra*) with respect to ferrocene (0.388 V).

Results and Discussion

The reaction of various palladium salts (*i.e.* Li_2PdCl_4, Cl_2Pd(1,5-cyclooctadiene), or $Cl_2Pd(NH_3)_2$) with n-propane thiol results in the quantitative formation of an amorphous orange solid. The ^1H NMR suggests that there are four inequivalent n-propyl groups belonging to a mixture of **I** and **II**. The compounds are readily soluble in solvents such as CH_2Cl_2 and $CHCl_3$, but are best recrystallized from pyridine. Thus, after standing at room temperature for 2 days, two types of compounds co-crystallized from pyridine, one as light orange prisms (**I**) and the other as dark orange cubes (**II**). Seeding the pyridine solution with either **I** or **II** still led to both compounds coming out of solution. ^1H NMR indicated that each crystal contained two types of inequivalent propyl groups.

Molecular Structure of I and II

X-ray crystallographic analysis of the light orange prisms revealed that they were the new mercaptide $Pd_8(S\text{-}nPr)_{16}$ (**I**). The unit cell was found to contain 8 independent $Pd_4(S\text{-}nPr)_8$ asymmetric units. The asymmetric unit is a half octamer, containing three full palladium atoms and two half palladiums which lie on a *C*2 symmetry axis. Figures 1 and 2 show views of **I** and its asymmetric unit (**Ia**), respectively. The complex can be described as a segmented octagonal toroid composed of eight approximately square planar palladium atoms, each being bridged by two n-propyl mercaptide groups. The Pd_8 ring forms a slightly distorted octagon (internal Pd–Pd–Pd bond angles average 128.3°) which is virtually planar, as are the coordinated sulfur rings above and below it.

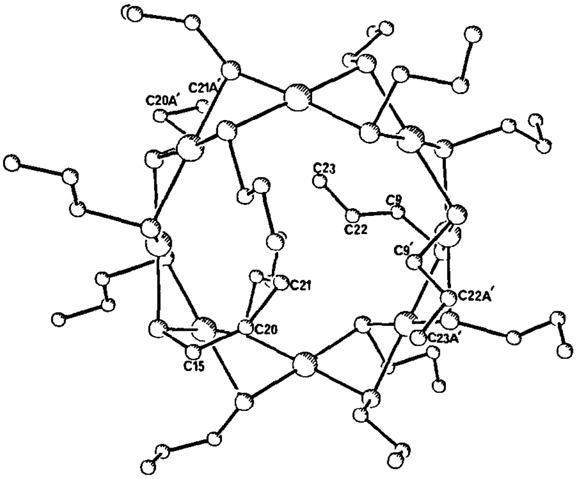

Fig. 1. Schematic view of $Pd_8(S\text{-}nPr)_{16}$ (I) normal to the Pd_8 ring plane (hydrogen and disordered carbon atoms have been omitted for clarity).

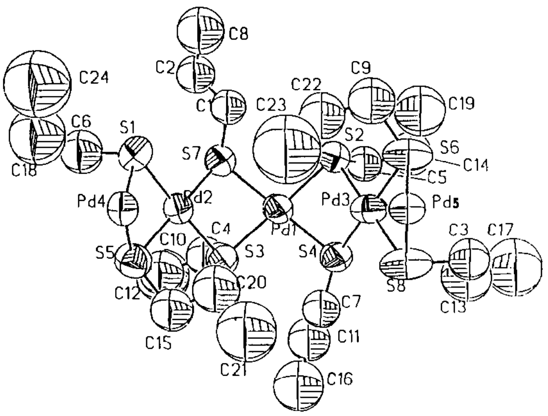

Fig. 2. Ortep view of the $Pd_4(S\text{-}nPr)_8$ (Ia) asymmetric unit parallel to the Pd_4 plane, with crystallographic numbering scheme (hydrogen and disordered carbon atoms have been omitted for clarity).

The basic structure of **I** is very similar to that of the related nickel mercaptide $Ni_8(S\text{-}CH_2CO_2Et)_{16}$ [5] (**III**). Figure 3 shows a schematic diagram which defines the angles described by the $M_8(S\text{-}R)_{16}$ geometry. The respective coordination geometries about Pd and Ni in **I** and **III** are identical, both being approximately square planar, where $\theta_1 \cong 82°$ and $\theta_2 \cong 98°$ (Fig. 3). The average Pd–S bond length in **I** is 2.370(6) Å as compared to an average Ni–S bond length of 2.191 Å in **III**. This difference leads to a larger non-bonded distance between metal atoms in **I** as compared to **III** (Pd–Pd ≅ 3.17 Å, Ni–Ni ≅ 3.05 Å), which ultimately results in the formation of M_8 rings with holes of 6.0 and 4.3 Å for **I** and **III**, respectively.

The pendent n-propyl side chains alternate in approximately axial and equatorial orientations in

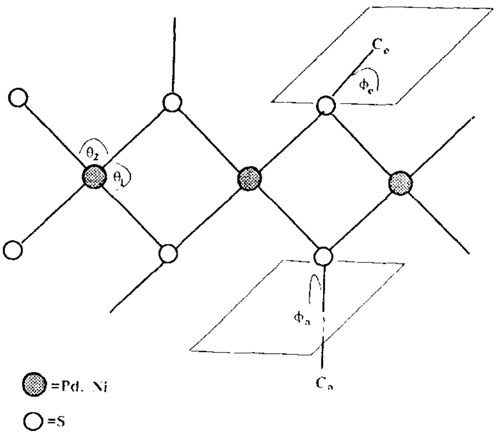

Fig. 3. Schematic fragment of the $M_8(S\text{-}R)_{16}$ ring system defining pertinent angles and planes. ϕa and ϕe represent the angles between the S–Ca and S–Ce vectors and a vector normal to the Pd–S–Pd plane. **I**: ϕa = 148°, ϕe = 20°; **II**: ϕa = 155°, ϕe = 18°; **I**, **II** and **III**: θ_1 = 82°, θ_2 = 98°.

TABLE III. Bond Lengths (Å) for $Pd_4(S\text{-}nPr)_8$ (**Ia**)

Pd(1)–Pd(2)	3.191(3)	Pd(1)–Pd(3)	3.151(3)
Pd(1)–S(2)	2.331(6)	Pd(1)–S(3)	2.320(6)
Pd(1)–S(4)	2.320(6)	Pd(1)–S(7)	2.314(5)
Pd(2)–S(1)	2.322(6)	Pd(2)–S(3)	2.321(6)
Pd(2)–S(5)	2.321(5)	Pd(2)–S(7)	2.320(5)
Pd(3)–S(2)	2.337(5)	Pd(3)–S(4)	2.324(6)
Pd(3)–S(6)	2.320(6)	Pd(3)–S(8)	2.352(5)
Pd(4)–S(1)	2.335(4)	Pd(4)–S(5)	2.323(6)
Pd(4)–S(1a)	2.335(4)	Pd(4)–S(5a)	2.323(6)
Pd(5)–S(6)	2.302(4)	Pd(5)–S(8)	2.324(6)
Pd(5)–S(6a)	2.301(4)	Pd(5)–S(8a)	2.323(6)
S(1)–C(6)	1.838(16)	S(2)–C(5)	1.822(14)
S(3)–C(4)	1.827(15)	S(4)–C(7)	1.831(14)
S(5)–C(15)	1.871(21)	S(6)–C(9)	1.833(29)
S(7)–C(1)	1.807(21)	S(8)–C(3)	1.918(15)
C(1)–C(2)	1.515(24)	C(2)–C(8)	1.512(36)
C(3)–C(13)	1.491(20)	C(4)–C(10)	1.496(20)
C(5)–C(14)	1.504(16)	C(6)–C(18)	1.503(37)
C(7)–C(11)	1.500(32)	C(9)–C(22)	1.502(37)
C(9)–C(22a)	1.505(58)	C(10)–C(12)	1.518(37)
C(11)–C(16)	1.511(31)	C(13)–C(17)	1.486(40)
C(14)–C(19)	1.482(46)	C(15)–C(20)	1.505(42)
C(15)–C(20a)	1.501(59)	C(18)–C(24)	1.479(65)
C(20)–C(21)	1.510(72)	C(22)–C(23)	1.507(58)
C(21a)–C(20a)	1.509(84)		
C(22a)–C(23a)	1.502(110)		

relation to the plane of the palladiums, except for four which are partially disordered and bend back into the center of the ring (in solution, the axial propyl groups most likely take turns moving rapidly in and out of the ring, since the ^1H NMR indicates only one type, together with one type of equatorial propyl group). Figure 1 shows that it is the C9–C22–C23 (A) and C15–C20–C21 (B) propyls which occupy the center of the ring. The last two carbons in each of these chains were disordered, and their *ca.* half S.O.F. counterparts, which radiate away from the ring center, are not shown. The orientations of these counterparts, however, can be seen upon observation of the symmetry equivalent side chains of A and B, C9′–C22A′–C23A′ and C15′–C20A′–C21A′, in which case the portions which occupy the ring center have been omitted. This ligand hole filling by the propyl groups is also seen in **III**, in which an ester group occupies the Ni_8 hole. Bond lengths and angles which are defined in Figs. 1 and 2, are given in Tables III and IV. X-ray crystallographic analysis of the dark orange crystals showed them to be reported [4] palladium mercaptide $Pd_6(S\text{-}nPr)_{12}$ (**II**). The crystal structure of this analogous hexagonal toroid was essentially identical to the previously reported complex.

It is interesting to note that the axial and equatorial propyl groups in **I** and **II** retain their inequivalence in solution, as evidenced in the ^1H and ^{13}C NMR spectra. In an earlier study on the nickel octamer [5] (**III**), Dance *et al.* pointed out that the geometry at sulfur in toroidal complexes $M_n(SR)_{2n}$ (Fig. 3) requires that as n increases, the difference between the pendent axial and equatorial R groups should decrease (ϕa and ϕe converge). Analysis of our crystallographic data proved this to be true, with ϕa = 148° and ϕe = 20° for **I**, while ϕa = 155° and ϕe = 18° for **II**. Hence, the propyl groups in the hexameric species (**II**) differ by 137°, while the propyl groups in the octamer (**I**) differ by only 128°. Comparison of the chemical shifts of the terminal methyl resonances in the ^1H NMR spectra of **I** and **II** also supports this suggestion. In complex **II** (n = 6) the axial and equatorial methyl triplets differ in chemical shift by 0.61 ppm, whereas in **I** (n = 8) the methyls are nearly equivalent. Their resonances differ by only 0.06 ppm. One would expect that at some temperature the axial and equatorial propyl groups in **I** or **II** would begin to interconvert via sulfur inversion. In cyclic platinum methyl mercaptides, heating at 60–90 °C causes exchange of inequivalent methyl groups by this process (which corresponds to a barrier of *ca.* 12–20 Kcal/mol) [7]. However, ^1H NMR measurements of either **I** or **II** in chlorobenzene at temperatures up to 95 °C showed no broadening of the resonances.

The fact that **I** and **II** always cocrystallize, suggested that there was an equilibrium between the two species in solution, and it should be possible to convert one into the other. We investigated this possibility by dissolving crystals of **I** or **II** in pyridine, and evaporating the solvents to dryness, leaving amorphous residues. ^1H NMR of the residues confirmed that in each case a mixture of **I** and **II** had formed, regardless of which ring one started with. **I** can be completely converted to **II**, however, by

TABLE IV. Bond Angles (°) for **Ia**

Pd(2)–Pd(1)–Pd(3)	126.4(1)	Pd(2)–Pd(1)–S(2)	130.3(2)
Pd(3)–Pd(1)–S(2)	47.6(1)	Pd(2)–Pd(1)–S(3)	46.6(2)
Pd(3)–Pd(1)–S(3)	129.1(1)	S(2)–Pd(1)–S(3)	174.7(2)
Pd(2)–Pd(1)–S(4)	133.9(1)	Pd(3)–Pd(1)–S(4)	47.3(2)
S(2)–Pd(1)–S(4)	82.1(2)	S(3)–Pd(1)–S(4)	98.0(2)
Pd(2)–Pd(1)–S(7)	46.6(1)	Pd(3)–Pd(1)–S(7)	134.3(2)
S(2)–Pd(1)–S(7)	98.7(2)	S(3)–Pd(1)–S(7)	81.4(2)
S(4)–Pd(1)–S(7)	178.1(2)	Pd(1)–Pd(2)–S(1)	131.6(1)
Pd(1)–Pd(2)–S(3)	46.6(1)	S(1)–Pd(2)–S(3)	176.2(2)
Pd(1)–Pd(2)–S(5)	133.3(1)	S(1)–Pd(2)–S(5)	82.7(2)
S(3)–Pd(2)–S(5)	96.9(2)	Pd(1)–Pd(2)–S(7)	46.4(1)
S(1)–Pd(2)–S(7)	99.2(2)	S(3)–Pd(2)–S(7)	81.2(2)
S(5)–Pd(2)–S(7)	177.1(2)	Pd(1)–Pd(3)–S(2)	47.5(1)
Pd(1)–Pd(3)–S(4)	47.2(1)	S(2)–Pd(3)–S(4)	81.8(2)
Pd(1)–Pd(3)–S(6)	133.8(2)	S(2)–Pd(3)–S(6)	97.0(2)
S(4)–Pd(3)–S(6)	176.5(2)	Pd(1)–Pd(3)–S(8)	132.4(2)
S(2)–Pd(3)–S(8)	179.2(2)	S(4)–Pd(3)–S(8)	98.5(2)
S(6)–Pd(3)–S(8)	82.7(2)	S(1)–Pd(4)–S(5)	82.4(2)
S(1)–Pd(4)–S(1a)	178.5(2)	S(5)–Pd(4)–S(1a)	97.6(2)
S(1)–Pd(4)–S(5a)	97.6(2)	S(5)–Pd(4)–S(5a)	177.8(2)
S(1a)–Pd(4)–S(5a)	82.4(2)	S(6)–Pd(5)–S(8)	83.8(2)
S(6)–Pd(5)–S(6a)	177.3(3)	S(8)–Pd(5)–S(6a)	96.2(2)
S(6)–Pd(5)–S(8a)	96.2(2)	S(8)–Pd(5)–S(8a)	179.7(3)
S(6a)–Pd(5)–S(8a)	83.8(2)	Pd(2)–S(1)–Pd(4)	90.4(2)
Pd(2)–S(1)–C(6)	103.9(8)	Pd(4)–S(1)–C(6)	105.9(6)
Pd(1)–S(2)–Pd(3)	84.9(2)	Pd(1)–S(2)–C(5)	106.2(6)
Pd(3)–S(2)–C(5)	102.4(5)	Pd(1)–S(3)–Pd(2)	86.9(2)
Pd(1)–S(3)–C(4)	103.7(5)	Pd(2)–S(3)–C(4)	107.2(6)
Pd(1)–S(4)–Pd(3)	85.5(2)	Pd(1)–S(4)–C(7)	110.6(6)
Pd(3)–S(4)–C(7)	108.4(6)	Pd(2)–S(5)–Pd(4)	90.7(2)
Pd(2)–S(5)–C(15)	108.6(6)	Pd(4)–S(5)–C(15)	107.5(8)
Pd(3)–S(6)–Pd(6)	90.2(2)	Pd(3)–S(6)–C(9)	113.0(8)
Pd(6)–S(6)–C(9)	110.5(6)	Pd(1)–S(7)–Pd(2)	87.0(2)
Pd(1)–S(7)–C(1)	112.6(5)	Pd(2)–S(7)–C(1)	110.0(5)
Pd(3)–S(8)–Pd(6)	88.9(2)	Pd(3)–S(8)–C(3)	101.3(5)
Pd(5)–S(8)–C(3)	101.3(6)	S(7)–C(1)–C(2)	110.4(12)
C(1)–C(2)–C(8)	107.7(15)	S(8)–C(3)–C(13)	106.4(13)
S(3)–C(4)–C(10)	111.0(11)	S(2)–C(5)–C(14)	122.4(13)
S(1)–C(6)–C(18)	116.8(17)	S(4)–C(7)–C(11)	107.0(11)
S(6)–C(9)–C(22)	109.3(24)	S(6)–C(9)–C(22a)	103.2(25)
C(22)–C(9)–C(22a)	146.9(36)	C(4)–C(10)–C(12)	99.4(17)
C(7)–C(11)–C(16)	110.0(16)	C(3)–C(13)–C(17)	97.5(21)
C(5)–C(14)–C(19)	109.4(20)	S(5)–C(15)–C(20)	107.6(22)
S(5)–C(15)–C(20a)	110.7(22)	C(20)–C(15)–C(20a)	139.9(27)
C(6)–C(18)–C(24)	108.1(27)	C(15)–C(20)–C(21)	106.4(40)
C(9)–C(22)–C(23)	152.8(33)	C(20a)–C(21a)–C(22b)	120.2(44)
C(15)–C(20a)–C(21a)	116.9(42)	C(9)–C(22a)–C(23a)	85.2(46)

heating it in pyridine at 80 °C for 12 h. We also found that interconversion between **I** and **II** can be achieved by simply adding a catalytic amount of Li_2PdCl_4 at room temperature to a solution of either complex. Since nickel mercaptides form Ni_4 cycles, we sought evidence of other ring sizes in our palladium system. The ^1H and ^{13}C NMR spectra of amorphous mixtures of the palladium mercaptides suggest that if other rings besides Pd_6 and Pd_8 are present, either the propyl groups have the same chemical shifts as the Pd_6 and Pd_8 species (which is unlikely), or they are present in under 5% of the total.

UV–Vis Spectroscopic Studies and Guest–Host Chemistry

The 6.0 and 4.7 Å holes in **I** and **II**, with their centrally directed d_{z^2} orbitals, render them to be promising candidates for the accommodation of cationic atoms or small molecules with cylindrical charge distribution. Complexation of a guest in either of the complexes should be easily detected by observing changes in the host's UV–Vis spectra, which showed several strong absorption maxima (see 'Experimental').

Attempts to complex various guests with **I** and **II** proved, unfortunately, to be fruitless. Salts such as $HgCl_2$, $MgCl_2$, and $ZnCl_2$ (the cations all of which have suitable van der Waals radii for complexation) as well as a number of small molecules such as monosubstituted alkynes gave no stable complexation products after reaction with **I** or **II** in solvents such as methanol and dichloromethane, as evidenced by the unchanged UV–Vis spectra. In the case of the octameric complex **I**, complexation of the guests may be discouraged by the four propyl groups moving in and out of the hole in solution, which also discouraged complexation in complex **III**. The general inertness of **I** and **II** was shown further by their failure to react with either CH_3I or I_2.

Finally, we investigated the electrochemistry of **I** and **II**. Cyclic voltammograms of the complexes were obtained at temperatures ranging from 25 to −60 °C. **I** displayed peak potentials at 0.77 and 1.09 V. Both appeared to be irreversible, one electron processes. Complex **II** displayed a reversible half wave potential at 0.77 V, and an irreversible oxidation wave at 1.09 V. Again, both were one electron processes. Reversibility was not enhanced in either case at lower temperatures. The reversibility of the 0.77 V oxidation wave in **II** *versus* **I** may reflect a greater stability of the Pd_6 ring.

Conclusions

The reaction of palladium salts with solubilizing thiols results in the formation of an equilibrium mixture of six and eight membered cyclic mercaptides and provides a quick entry into inorganic molecular toruses. The high solubility of these toroidal complexes allows for their structures to be further studied by standard spectroscopic methods. The fact that guests could not be complexed in the center of the rings remains a challenge, but is not in disagreement with previous studies [5] on related mercaptides.

Supplementary Material

Tables of anisotropic thermal parameters for the palladium and sulfur atoms, hydrogen atom coordinates, and a listing of observed and calculated structure factors are available from the author on request.

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References

1 N. R. Kunchar, *Nature, 204,* 468 (1964); P. J. Blower and J. R. Dillworth, *Coord. Chem. Rev., 76,* 121 (1987).
2 K. A. Jensen, *Z. Anorg. Allg. Chem., 252,* 227 (1944).
3 W. Gaete, J. Ros, X. Solans, M. Font-Altaba and J. L. Brianso', *Inorg. Chem., 23,* 39 (1984).
4 N. R. Kunchar, *Acta Crystallogr., Sect. B, 24,* 1621 (1968).
5 I. G. Dance, M. Scudder and R. Secomb, *Inorg. Chem., 24,* 1201 (1985).
6 L. F. Dahl, P. Woodward, E. Abel and B. Crosse, *J. Am. Chem. Soc., 87,* 5251 (1965).
7 E. W. Abel, R. P. Bush, F. J. Hopton and C. R. Jenkins, *J. Chem. Soc., Chem. Commun.,* 58 (1966); P. Haake and P. C. Turley, *J. Am. Chem. Soc., 89,* 4611 (1967).