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INORGANIC RINGS: EIGHT-MEMBERED Pd_4S_4 RING IN $[Pd_4Cl_4\{1\text{-}S\text{-}2\text{-}SCH_2COOMe\text{-}C_6H_4\text{-}\kappa^2 S,S'\}_4]$

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ABSTRACT. Under solvothermal conditions in methanol the mononuclear complex *cis-rac*-$[PdCl_2\{1,2\text{-}(HOOCCH_2S)_2C_6H_4\text{-}\kappa^2 S,S'\}]$ (2) reacted to give the tetranuclear palladium(II) complex $[Pd_4Cl_4\{1\text{-}S\text{-}2\text{-}SCH_2COOMe\text{-}C_6H_4\text{-}\kappa^2 S,S'\}_4]$ (3). The molecular structure of 3 was investigated by single-crystal X-ray structure analysis.

Keywords: *palladium(II) complex, solvothermal, S-dealkylation, X-ray crystallography, inorganic ring*

INTRODUCTION

A topic of current interest in recent years has been the chemistry of coordination polymers due to their fascinating architectures and applications in many fields like catalysis, gas storage, magnetism, ion exchange, and nonlinear optics [1-5]. One of the most widely used methods to synthesize coordination polymers is molecular self-assembly [6, 7], but the controlling factors and experimental conditions for the preparation of such polymers are not yet completely understood [8, 9]. Therefore, in recent years rational synthetic approaches for the assembly of target structures from molecular building blocks have been considered. The key step in the rational approach is the design of suitable molecular building blocks which can direct the formation of the desired architecture and functionality of the target compound. In this context, we have previously reported several mononuclear transition metal complexes of 1,2-phenylenebis(thio)diacetic acid as potential building blocks for the rational synthesis of coordination polymers [10]. Here we present the unexpected formation of tetranuclear palladium(II) complex $[Pd_4Cl_4\{1\text{-}S\text{-}2\text{-}SCH_2COOMe\text{-}C_6H_4\text{-}\kappa^2 S,S'\}_4]$ (**3**) under solvothermal conditions from mononuclear *cis-rac*-$[PdCl_2\{1,2\text{-}(HOOCCH_2S)_2C_6H_4\text{-}\kappa^2 S,S'\}]$ (**2**) under solvothermal conditions in methanol.

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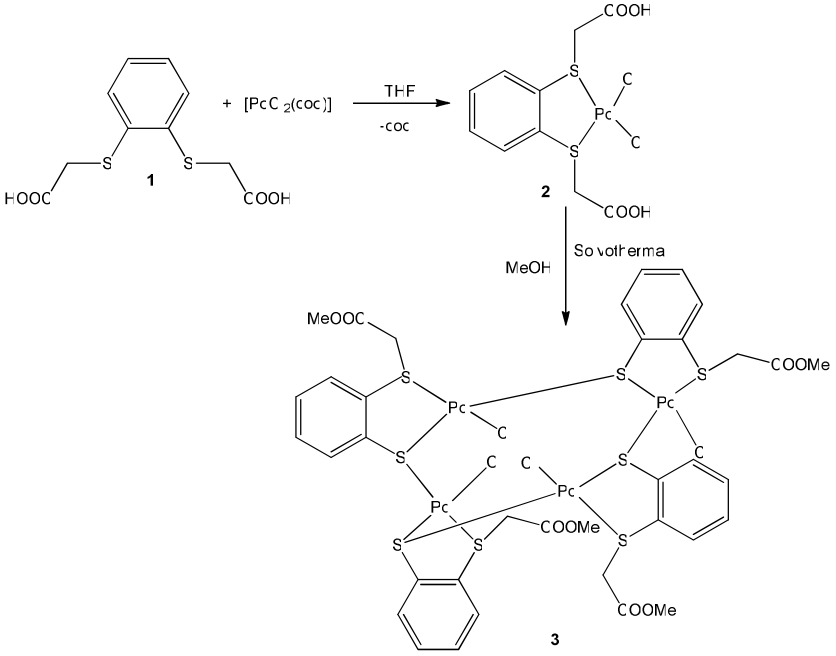
RESULTS AND DISCUSSION

Complex **2** was obtained according to a previously published method [10] from 1,2 –phenylene phenylenebis(thio)diacetic acid [11] and $[PdCl_2(cod)]$ (cod = 1,5-cyclooctadiene). Heating a highly diluted methanol solution of **2** under solvothermal conditions at 120 °C for 12 hours and then slowly cooling to room temperature gave dark orange crystals of tetranuclear complex **3** (Scheme 1). Unfortunately, complex **3** could not be reproduced under solvothermal conditions or in refluxing methanol.



Scheme 1

The formation of tetranuclear sulfido-bridged palladium(II) complex **3** may have occurred by methylation of the carboxylato groups followed by elimination of chloromethyl acetate. Similar *S*-dealkylation of some palladium(II) complexes was observed for the series $[MX_2(1\text{-}AsMe_2\text{-}2\text{-}MeSC_6H_4\text{-}\kappa S)_2]$ (M = Pt, Pd; X = Cl, Br, I; R = CH_3). The reaction gave metal complexes $[M(1\text{-}AsMe_2\text{-}2\text{-}SC_6H_4\text{-}\kappa^2 As,S)_2]$ in which the ligand is strongly bonded to the metal center through the sulfur and arsenic atoms [12].

Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Each palladium atom is fourfold-coordinated in a square-planar fashion by three sulfur atoms, two of which belong to the same ligand and the third to a ligand of another palladium complex unit (Figure 1).

The coordination sphere is completed by one chloro ligand. The four 1-S-2-$SCH_2COOMeC_6H_4$ ligand molecules differ from each other in that the four pendant arms (CH_2COOMe) exhibit different conformations with $C_{aromatic}$-S-CH_2-COOMe torsion angles of 58.68(1), 48.46(1), 65.80(7), and 43.32(2)°, respectively.

The four palladium atoms alternate with four bridging thiolato groups and together form an inorganic eight-membered ring in a boat–boat conformation due to short Pd(1)···Pd(2) (3.1589(8) Å) and Pd(3)···Pd(4) (3.2401(8) Å) contacts (Figure 2). These contacts suggest interactions between the palladium atoms, but they are significantly longer than the Pd–Pd bonds observed in related compounds, e.g., 2.581(3) Å in $[\{Pd(\mu\text{-}SC_6F_5)(\mu\text{-}dppm)Pd\}(\mu\text{-}SC_6F_5)]_4{\cdot}2O(C_2H_5)_2$ (dppm = diphenylphosphinomethane) [13] and 2.7247(5) Å in $[Pd_2(dtp)_4]$ (dtp = dithiopropionate, $C_2H_5CS_2^-$), which exhibits one-dimensional metal-dimer chains of $[Pd_2(dtp)_4]$ with moderate interdimer contacts (3.428(2) Å) [14]. Shorter Pd···Pd contacts (2.942(2) Å) were observed in $[Pd_2(\mu\text{-}N\text{-}S\text{-}pyS\text{-}\kappa^2 N,S)_2Cl_2(PMe_3)_2]$ (pyS = μ-pyridine-2-thiolate) [15].

The Pd–S bond lengths (2.244(2) Å to 2.313(2) Å) are longer than the Pd–S bonds in complex **2** but are similar to Pd–S bonds observed in related compounds [13-15].

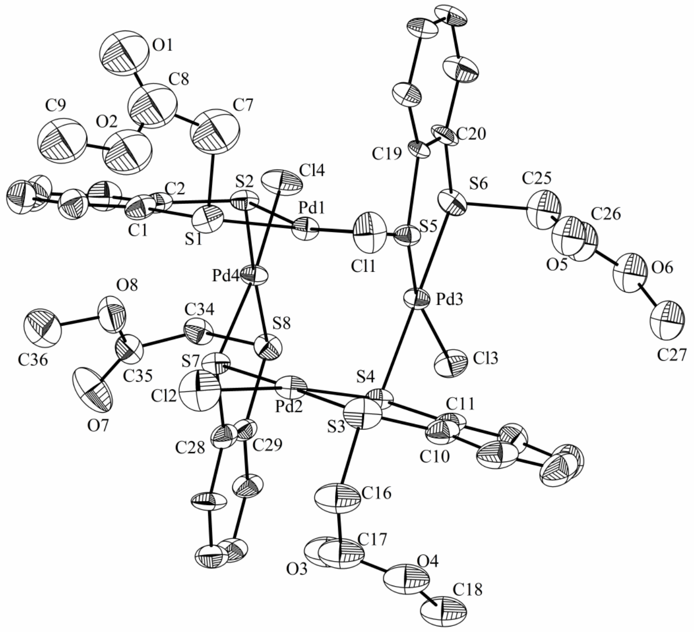


Figure 1. Molecular structure of **3** with atom labeling (thermal ellipsoids at 50% probability; hydrogen atoms omitted for clarity).

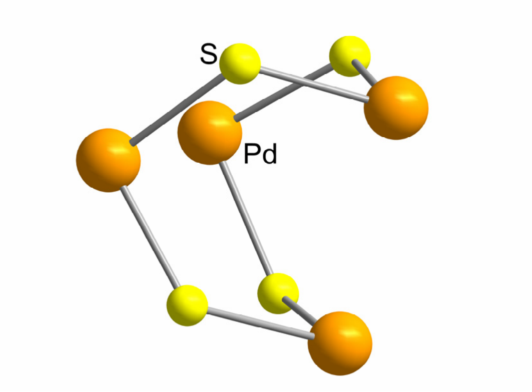


Figure 2. Central Pd_4S_4 ring showing boat–boat conformation.

Table 1. Selected bond lengths (Å) and angles (°) in **3**

Pd(1)-S(1)	2.285(2)	S(1)-Pd(1)-S(2)	89.64(7)
Pd(1)-S(2)	2.248(2)	S(2)-Pd(1)-S(5)	92.41(7)
Pd(1)-S(5)	2.311(2)	S(1)-Pd(1)-S(5)	177.14(7)
Pd(1)-Cl(1)	2.341(2)	S(2)-Pd(1)-Cl(1)	167.69(8)
Pd(2)-S(3)	2.282(2)	S(3)-Pd(2)-S(4)	89.76(8)
Pd(2)-S(4)	2.245(2)	S(4)-Pd(2)-S(7)	90.99(7)
Pd(2)-S(7)	2.329(2)	S(4)-Pd(2)-Cl(2)	172.75(8)
Pd(2)-Cl(2)	2.327(2)	S(7)-Pd(2)-Cl(2)	91.29(7)
Pd(3)-S(4)	2.321(2)	S(5)-Pd(3)-S(6)	89.25(7)
Pd(3)-S(5)	2.253(2)	S(4)-Pd(3)-S(5)	93.70(7)
Pd(3)-S(6)	2.284(2)	S(4)-Pd(3)-S(6)	176.85(7)
Pd(3)-Cl(3)	2.334(2)	S(5)-Pd(3)-Cl(3)	168.31(7)
Pd(4)-S(2)	2.313(2)	S(2)-Pd(4)-S(7)	91.38(7)
Pd(4)-S(7)	2.248(2)	S(2)-Pd(4)-S(8)	177.69(7)
Pd(4)-S(8)	2.275(2)	S(2)-Pd(4)-Cl(4)	89.73(7)
Pd(4)-Cl(4)	2.335(2)	S(8)-Pd(4)-Cl(4)	88.99(7)

In the network, the molecules of **3** have an edge-to-face arrangement (Figure 3). Moreover, there are π–π stacking interactions between two phenyl rings belonging to two different molecules of **3** even though the phenyl rings are not strictly parallel to each other. The rings have an offset face-to-face arrangement with a distance between the centroids defined by the phenyl rings of 4.285 Å and an offset of 2.55.

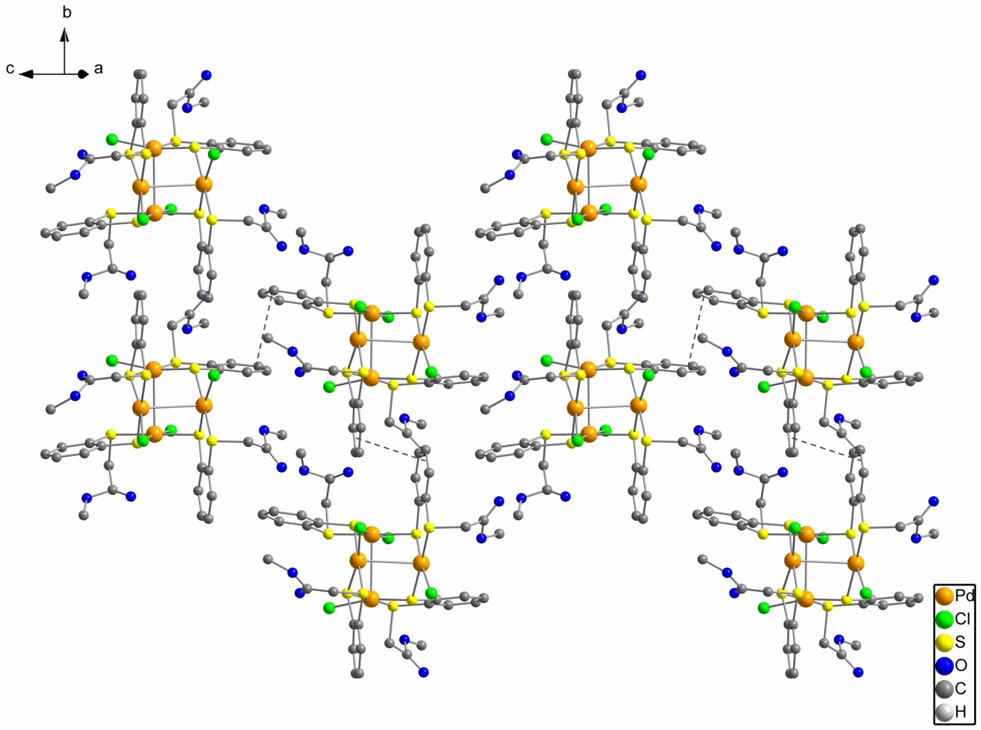


Figure 3. Edge-to-face arrangement and π–π stacking interactions of phenylene rings in **3** (view along the *a*-axis, hydrogen atoms omitted for clarity).

CONCLUSIONS

Under solvothermal conditions the mononuclear palladium(II) complex **2** eliminates chloro acetic acid (or chloromethyl acetic acid after esterification) to give a tetranuclear palladium(II) complex. The structure of the tetranuclear complex was determined by X-ray crystallography.

EXPERIMENTAL SECTION

The data of **3** were collected on a CCD Oxford Xcalibur S ($\lambda(Mo_{K\alpha})$ = 0.71073 Å) in ω and Φ scan modes with $Mo_{K\alpha}$ radiation (λ 0.71073 Å). Data reduction was performed with CrysAlis Pro including the program SCALE3 ABSPACK for empirical absorption correction [16]. All structures were solved by direct methods [17] and the refinement of all atoms was performed with SHELXL-97 [17]. Structure figures were generated with DIAMOND-3 [18]. Some fragments of the ester moieties are disordered and were refined over split positions with constrained geometry and fixed atomic displacement parameters (SADI and EADP instructions).

A summary of the data collection, structure solution, and refinement details for compound **3** is given in Table 2. CCDC 805586 (**3**) 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.

Table 2. Crystal Data and Structure Refinement for **3**

Empirical formula	**$C_{36}H_{36}Cl_4O_8Pd_4S_8$**
M	1420.53
T/K	130(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	20.4269(8)
b/Å	10.8202(4)
c/Å	21.6073(9)
β/°	109.804(4)
V/Å^3	4493.3(3)
Z	4
$D_{\mathrm{calcd.}}$/Mg m^{-3}	2.100
μ/mm^{-1}	2.235
F(000)	2784
Reflections collected	65370
Independent reflections	8189 [R(int) = 0.1104]
Restraints/parameters	19/501
Goodness of fit on F^2	0.896
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0464$, $wR2 = 0.0697$
R indices (all data)	$R1 = 0.1053$, $wR2 = 0.0808$
Largest diff. peak and hole/e Å$^{\mathrm{I\,I}3}$	1.477 and -1.343

Synthesis of [Pd_4Cl_4\{1-S-2-SCH_2COOMe-C_6H_4-κ^2S,S'\}$_4$] (3)

A solution of complex **2** (0.004 g, 0.009 mmol) in MeOH (4 mL) was placed in a stainless steel container, which was heated gradually over 12 hours to 120 °C, maintained at this temperature for a further 12 hours, and slowly cooled to room temperature over 12 hours. Dark orange crystals of **3** were obtained directly from the reaction mixture.

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REFERENCES

1. A.Y. Robin, K.M. Fromm, *Coord. Chem. Rev.*, **2006**, *250*, 2127; S. Kitagawa, K. Uemura, *Chem. Soc. Rev.,* **2005**, *34*, 109; S. Bureekaev, S. Shimomuram, S. Kitagawa, *Sci. Technol. Adv. Mater.,* **2008**, *9*, 014108.
2. B. Moulton, M.J. Zawarotko, *Chem. Rev.,* **2001**, *101*, 1629; S. Noro, S. Kitagawa, T. Akutagawa, T. Nakamura, *Progress in Polymer Science*, **2009**, *34*, 240.
3. M.J. Rosseinsky, *Microporous and Mesoporous Materials*, **2004**, *73*, 15; J.L.C. Rowsell, O.M. Yaghi, *Microporous and Mesoporous Materials*, **2004**, *73*, 3.
4. A.K. Cheetham, C.N.R. Rao, R.K. Feller, *Chem. Commun.*, **2006**, 4780.
5. B.F. Abrahams, B.F. Hoskins, R. Robson, *J. Chem. Soc., Chem. Commun.*, **1990**, 762.
6. D. Braga, F. Grepioni, G.R. Desiraju, *Chem. Rev.*, **1998**, *98*, 1375.
7. A.M. Spokoyny, D. Kim, A. Sumrein, C.A. Mirkin, *Chem. Soc. Rev.*, **2009**, *38*, 1218.
8. S.L. James, *Chem. Soc. Rev.*, **2003**, *32*, 276.
9. D.J. Tranchemontagne, J.L. Mendoza-Cortes, M. O'Keeffe, O.M. Yaghi, *Chem. Soc. Rev.*, **2009**, *38*, 1257.
10. C. Berghof, I.G. Grosu, P. Lönnecke, S. Goméz-Ruiz, L. Silaghi-Dumitrescu, E. Hey-Hawkins, *Inorg. Chim. Acta*, in press, **2011**, doi: 10.1016/j.ica.2010.12.004.
11. A.B. Kyte, K.A. Owens, I.O. Sutherland, R.F. Newton, *J. Chem. Soc. Perkin Trans.,* **1987**, *1*, 1921; T. Wei, J. Chen, X. Wang, Y. Zhang, L. Wang, *Syn. Comm.*, **1996**, *26*, 1447.
12. J.P. Beale, N.C. Stephenson, *Acta Cryst.*, **1971**, *B27*, 73; L.F. Lindoy, S.E. Livingstone, T.N. Lockyer, *Inorg. Chem.*, **1967,** *8*, 652; J.P. Beale, N.C. Stephenson, *Acta Cryst.*, **1970**, *B26*, 1655.
13. R. Usón, J. Forniés, L.R. Falvello, M.A. Usón, I. Usón, S. Herrero, *Inorg. Chem.*, **1993**, *32*, 1066.
14. A. Kobayashi, T. Kojima, R. Ikeda, H. Kitawaga, *Inorg. Chem.*, **2006**, *45*, 322.
15. J.H. Yamamoto, W. Yoshida, C.M. Jensen, *Inorg. Chem.*, **1991**, *30*, 1353.
16. CrysAlisPro: Data collection and data reduction software package, Varian, Inc. including SCALE3 ABSPACK: Empirical absorption correction using spherical harmonics.
17. SHELX97: Includes SHELXS97, SHELXL97; G.M. Sheldrick, (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany.
18. DIAMOND 3: K. Brandenburg, Crystal Impact GbR, Bonn, Germany.