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Inorganica Chimica Acta 358 (2005) 213-216

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# An unusual *cis*-phosphonodithioato Pd(II) complex in an extensive hydrogen bonding 3D network

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Received 12 May 2004; accepted 10 July 2004 Available online 12 August 2004

## Abstract

The P–N bond hydrolysis of the 4-methoxyphenyl-ammoniumethylamido-phosphonodithioato ligand on complexation to Pd<sup>II</sup> leads to the first example of a Pd-phosphonodithioato complex in a *cis* configuration, stabilised in the solid state by an extended network of hydrogen bondings involving the released ethylenediamine and a water molecule. © 2004 Elsevier B.V. All rights reserved.

Keywords: Supramolecular chemistry; Phosphonodithioato ligands; Pd; X-ray crystal structure

## 1. Introduction

After 30 years of its origin [1], crystal engineering is a research field at the best of its blossoming, and it is attracting an increasing number of scientists on the international scene. In fact, due to the contributions deriving from every branch of chemistry, modern crystal engineering embraces now traditionally separated disciplines such as organic, inorganic and organometallic synthetic chemistry, as well as theoretical and physical chemistry, and materials science. The crystal engineering philosophy is that of utilising non-covalent interactions and/or coordination bonds to generate supramolecular structures, which respond to predetermined features [2]. Inorganic supramolecular chemistry has now become a rapidly expanding area [3], since the incorpora-

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tion of metal ions into extended networks gives access to a variety of physical properties [4] such as optical properties, electrical conductivity and magnetism [5]. Existing design strategies for the synthesis of extended inorganic networks follow two principal methods based on the different nature of the interactions responsible for networking. In one approach, which is the more frequently used, coordinative covalent bonds engaged between transition-metal ions and various organic "linkers", such as 4,4'-bipyridine, propagate the coordination geometry into infinite architectures of various dimensionality and topology [6]. The other method exploits weaker intermolecular forces (particularly  $\pi - \pi$ interactions, hydrogen bonding, and halogen bonding) as a guide to the assembly of molecular coordination complexes into extended networks [7]. We present here an innovative approach based on the "one-pot" self-assembly of a 3D extended network by a combination of coordinative and hydrogen bonds, starting from a ligand formed in situ by P-N bond hydrolysis during the reaction with the metal ion.

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# 2. Experimental

#### 2.1. Materials and methods

All solvents and Lawesson's Reagent (1) are commercially available and were used as received. Elemental analyses were performed with an EA-1108 CHNS-O Fisons instrument. Infrared spectra were recorded with a Bruker IFS55 Spectrometer at room temperature. NMR spectra were recorded with a Varian Unity Inova 400-MHz instrument. <sup>31</sup>P NMR chemical sifts were calibrated indirectly through the 85% H<sub>3</sub>PO<sub>4</sub> peak ( $\delta = 0.0$ ).

# 2.2. Synthesis

 $[(4-MeOPh)(^{+}NH_3CH_2CH_2NH)PS_2^{-}]$  (2) was synthesised by reacting 1 and ethylenediamine (en) according to a procedure previously outlined [8]. 3 was synthesised by reacting 2 (0.52 g, 2.0 mmol) with K<sub>2</sub>PdCl<sub>4</sub> (0.33 g, 1.0 mmol) in 70 mL of a CH<sub>3</sub>CN:H<sub>2</sub>O 1:1 mixture. After refluxing for 1 h, the reaction mixture was cooled to room temperature and the orange crystalline product was filtered off. Yield 0.32 g (51.4%). Elemental Anal. Calc./found: for C<sub>16</sub>H<sub>26</sub>- $N_2O_5P_2PdS_4$ : C, 31.2 (30.8); H, 4.0 (4.2); N, 4.7 (4.5); S, 20.8 (20.6)%. IR: 2056 s(br), 1630 m, 1601 vs, 1568 s, 1502 vs(br), 1456 ms, 1437 m, 1405 m, 1344 mw, 1309 m, 1297 ms, 1266 s, 1254 ms, 1179 s, 1118 s, 1085 s, 1071 s, 1022 vs(br), 823 vs, 800 ms, 718 w, 650 ms, 633 mw, 590 s, 551 s, 520 m, 412 mw, 404 mw, 371 w, 329 w, 313 w, 300 w cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO solution):  $\delta = 8.55$  (br), 8.15 (m), 7.75 (m), 7.10 (d), 6.99 (d), 3.92 (m), 3.88 (m), 3.22 (s), 2.62 (s) ppm. <sup>31</sup>P NMR (CDCl<sub>3</sub> solution):  $\delta$  = 74.5, 75.6 ppm.

#### 2.3. X-ray crystallographic studies

Crystals of 3 were obtained by slowly cooling a solution of 3 in CH<sub>3</sub>CN/H<sub>2</sub>O 1:1 mixture. A crystal sample was mounted on glass fibre in a random orientation and collected at room temperature on an Enraf-Nonius CAD4 diffractometer. Graphite monochromatised Mo Ka radiation ( $\lambda = 0.71073$  Å) was used with the generator working at 50 kV and 30 mA. Cell parameters and orientation matrix were obtained from least-squares refinement on 25 reflections measured in the range  $9.40 < \theta < 15.42^{\circ}$ . Three reference reflections were recollected to have a monitoring of the crystal decay, which was not observed. An absorption correction was applied using the  $\psi$ -scan routine [9]. The structure was solved by direct methods (SIR 97) [10] and refined on  $F^2$  using the SHELX-97 [11] program implemented in the WINGX suite [12]. Anisotropic displacement parameters were assigned to all non-hydrogen atoms. The hydrogen atoms, all seen in a difference Fourier map, were included in the structure model riding on their pertinent atoms; those of the water molecule were instead refined with constraints.

#### 2.4. Crystal data for 3

C<sub>16</sub>H<sub>26</sub>N<sub>2</sub>O<sub>5</sub>P<sub>2</sub>PdS<sub>4</sub>, M = 622.97, monoclinic, space group *Pc*, a = 7.080(2), b = 16.250(3), c = 10.719(3) Å,  $\beta = 95.39(2)^{\circ}$ , U = 1227.8(5) Å<sup>3</sup>, Z = 2,  $D_c = 1.685$ g cm<sup>-3</sup>,  $\mu$ (Mo K $\alpha$ ) = 1.256 mm<sup>-1</sup>, 2370 reflections collected, 2128 unique, R = 0.0173,  $wR_2 = 0.0431$  [2036 reflections having  $I > 2\sigma(I)$ ]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 246270. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code +1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

#### 3. Results and discussion

The reaction between diorgano-dithiadiphosphetane disulfides  $(RPS_2)_2$  (R = 4-MeOPh, Ph) and alcohols [13,14] or amines [13] R'XH (X = NH, O; R = alkyl) has recently been described.



The resulting phosphonodithioato anions R(R'X)- $PS_2^-$  (R'Xpdt) react with Group 10 metal ions giving square-planar phosphonodithioato complexes  $[M(R'-Xpdt)_2]$  (M = Ni, Pd, Pt) that generally crystallize as *trans*-isomers. Recently, from the reaction between Lawesson's reagent [R = 4-MeOPh, 1] and ethylenediamine (*en*) the expected amidophosphonodithioato anion was obtained as inner salt [(4-MeOPh)(<sup>+</sup>NH<sub>3</sub>-CH<sub>2</sub>CH<sub>2</sub>NH)PS<sub>2</sub><sup>-</sup>, **2**] featuring the proton on the amino group not bound to the phosphorous atom [8].

Reaction of **2** with K<sub>2</sub>PdCl<sub>4</sub> affords crystals of  $[(HOpdt)_2Pd \cdot en \cdot H_2O]_{\infty}$  (**3**), whose crystal structure is made up of discrete molecules of  $cis[(HOpdt)_2Pd]$ , en, and water, held together by an extended network of hydrogen bonds. The unusual complex cis-bis[(4-meth-oxyphenyl)-hydroxyl-phosphonodithioato]Pd (Fig. 1) contains a palladium ion coordinated to two HOpdt anions through the sulfur atoms in a square-planar arrangement, with an average Pd–S distance of 2.339 Å. The HOpdt anions are formed in situ by hydrolytic cleavage of the P–N bond of **2** and substitution of the en moiety with a hydroxyl group. The PdS<sub>4</sub> core is essentially planar with maximum deviations from the average plane of 0.05 Å. The distinctive feature of this complex is the



Fig. 1. Herringbone-like ribbons formed by coupled chains built by propagating **3** along the *c* direction. Besides the hydrogen bonds described in the text, a secondary weak hydrogen bond between N2 and H(O3') [H···N 2.40 Å], as well as a P1···H(N1") contact (2.93 Å) contribute to bind the units into chains. Non-interacting hydrogen atoms and N2 atoms have been omitted for clarity. ': x, y, -1 + z; ": x, y, 1 + z; ": x, 1-y, -1/2 + z.

*cis* arrangement of the 4-MeOPh appendages with respect to the coordination plane. In fact, even though the existence of *cis*-phosphonodithioato complexes was demonstrated by Fackler and Thompson [15], who explored the *cis-trans* isomerisation of the Ni<sup>II</sup>, Pd<sup>II</sup>, and

Pt<sup>II</sup> complexes of O-ethyl-phenylphosphonodithioato  $[EtO(Ph)PS_2]^-$  anion in several organic solvents by <sup>1</sup>H NMR spectroscopy, these complexes commonly crystallise only in a trans configuration. To the best of our knowledge, the other unique case of phosphonodithioato complex isolated in the solid state only in a cis configuration is cis-bis[(4-methoxyphenyl)-hydroxyl-phosphonodithioato]Ni, recently reported [8], which is isostructural with compound 3. Although  $C_{2v}$ ,  $C_s$  and  $C_2$  symmetries are accessible to the *cis*-isomer, the molecule adopts an asymmetric conformation in the crystal. While the P2 atom lies approximately in the coordination plane [distance 0.108(1) Å], P1 is significantly displaced on the side of its phenyl ring [distance 0.465(1) Å]. In addition, the phenyl ring is oriented to be almost coplanar with the O3–P1–C8 plane [dihedral angle 12.3°]. The simultaneous occurrence of these two features suggests that they co-operate in optimising the  $Pd \cdots H(C9)$  contact [3.20 Å] in order to establish a weak agostic-type interaction. At the same time, the hydrogen bonded to C13 is engaged in the O3 $\cdot \cdot \cdot$ H(C13) contact that adds stability and helps in maintaining the most favourable orientation of the phenyl group. An analysis of the conformation of the phenyl ring bonded to P2 also reveals a special orientation, being the phenyl almost coplanar with the S3P2C1 plane [dihedral angle 6.4°]. This orientation minimises the S3...H(C6) contact [2.83 A], which corresponds to an attractive sulfur-hydrogen interaction.

Units of [(HOpdt)<sub>2</sub>Pd] are bridged head to tail by ethylenediamine molecules to give infinite 1D chains running along the *c* direction (Fig. 1). The H-bonds between the P–OH moieties and the N1H<sub>2</sub> amino groups hold together the infinite chains  $[O3' \cdots N1 \ 2.877(5),$  $O4 \cdots N1 \ 2.667(6)$ ; (N1)H $\cdots O3' \ 2.00(6)$ , (O4)H $\cdots N1 \ 1.85(6)$  Å]. Also the aromatic substituents at the phosphorus atoms, which are disposed on either side of the chains, bridge adjacent molecules of [(HOpdt)<sub>2</sub>Pd]



Fig. 2. 2D view (*bc* plane) of [(HOpdt)<sub>2</sub>Pd · *en* · H<sub>2</sub>O]<sub> $\infty$ </sub> showing alternate inorganic (shaded) and organic (clear) layers interacting through H···ring centroid type C–H·· $\pi$  contacts (2.96 Å). Non-interacting hydrogen atoms have been omitted for clarity.

through CH··· $\pi$  contacts (2.96 Å). Pairs of infinite symmetry-related chains arranged on parallel planes shifted by c/2 are coupled together into infinite herringbone-like ribbons. The water molecules play the main role in forming these ribbons by H-bonding the S4 atom of one chain [O5···S4 3.204(4), H···S 2.40 Å, a] with the opposite O3<sup>'''</sup> atom [O3<sup>'''</sup>···O5 2.839(5), (O5)H···O3<sup>'''</sup> 1.97 Å, b]. The ribbons are interpenetrated by interacting through H···ring centroid type C–H··· $\pi$  contacts [16] forming 2D sheets (bc planes) as shown in Fig. 2. These sheets pack on top of each other along the axis a by interacting through hydrogen bonds, involving the N2H<sub>2</sub> amino group and the O3 and O5 atoms of neighbouring sheets [N2···O3 2.764(5); N2···O5 2.800(6); N2H···O3/O5 1.95/1.92 Å].

# 4. Conclusions

In conclusion, the mutual recognition between  $cis[(HOpdt)_2M]$  complexes (M = Ni [8], Pd (3)) and ethylenediamine occurs at the second coordination sphere level, leading to the supramolecular assembly  $[(HOpdt)_2M \cdot en \cdot H_2O]_{\infty}$ , promoted by the hydrogen bonding interactions. The crystallisation process seems to be the driving force for the unusual hydrolytic P–N bond cleavage with successive release of *en* and formation of the *cis*[(HOpdt)\_2M] complex. The possibility of incorporating different metal ions into extended hydrogen-bonded network starting from a single material represents a novel one-pot synthetic route to the crystal engineering of supramolecular materials based on hydrogen-bondings involving coordination compounds and organic molecules.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.ica.2004.07.019.

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