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# Supramolecular assemblies of *cis*-palladium complexes dominated by C-H···Cl interactions

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#### Abstract

Two *cis*-related palladium(II) complexes [PdCl<sub>2</sub>(PPh<sub>3</sub>)(tu)] (1) and [PdCl<sub>2</sub>(tmen)] (2) {PPh<sub>3</sub> = triphenylphosphine, tu = thiourea, tmen = N, N, N', N'-tetramethylethylenediamine} have been synthesized and characterized by elemental analysis, IR and NMR spectroscopies, and single crystal X-ray diffraction. In 1, N-H···Cl hydrogen bonds are responsible for the formation of a dimer which connects to an adjacent one through weak C-H···Cl interactions, yielding 1D tapes. The crystal packing of compound 2 consists of zigzag ribbons of [PdCl<sub>2</sub>(tmen)] self-assembled by C-H···Cl hydrogen bonds which also holds the chains together, giving rise to a 2D layered structure.

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The design of new solid state architectures with peculiar properties involving the self-assembly of molecular building blocks into sophisticated supramolecules via non-covalent intermolecular interactions has become one of the most exciting topics in current chemistry [1]. Among the intermolecular forces, hydrogen bonds have been considered as the most powerful organizing element in molecular assembly due its highly selective and directional character. Besides the conventional strong hydrogen bonds of the O-H···O, N-H···O, and N-H···N type, weak forces such as C-H···X (X = O, N, Cl) also play an important role in determining crystal structure stability [2].

In recent years, some authors have obtained detailed information regarding the properties of halogens as hydrogen bond acceptor as well the reproducibility of such weak interactions in constructing supramolecular architectures [3]. Particularly, special attention has been devoted to the C-H···Cl interactions since the HB acceptor capability of terminal metal-bound chlorine (M-Cl) is stronger than their C-Cl analogues [4]. Therefore, the C-H···Cl-M hydrogen bonding can be used to assembly transition-metal based building blocks into well-defined structures. In previous investigations, we have successfully obtained transition-metal based supramolecular species based on the self-assembly of [PdX<sub>2</sub> (3,5-dimethylpyrazole)<sub>2</sub>] building blocks via intermolecular hydrogen bonds of the N-H···X-Pd type (X = NCS, N<sub>3</sub>) [5].

Extending our interest in the coordination and supramolecular chemistry of palladium complexes containing halides and pseudohalides as co-ligands [6], we wish to report the synthesis and crystal structures of two *cis*-related palladium(II) complexes [PdCl<sub>2</sub>(PPh<sub>3</sub>)(tu)] (1) and [PdCl<sub>2</sub>(tmen)] (2) {PPh<sub>3</sub> = triphenylphosphine, tu = thiourea, tmen = N, N, N', N'-tetramethylethylenediamine} in which the C-H···Cl-Pd interactions play an important role in the crystal packing of the two new structures. Both

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compounds have been synthesized [7] and characterized by X-ray crystallographic methods [8].

In the IR spectrum of 1, recorded as KBr pellet, the vNH and  $\delta$ NH<sub>2</sub> vibrational modes of thiourea ligand were found as a broad band extending from 3339 to  $3182 \text{ cm}^{-1}$ and a strong absorption at  $1625 \text{ cm}^{-1}$ , respectively. Some characteristic IR absorptions of coordinated PPh<sub>3</sub> were observed at  $3056 \text{ cm}^{-1}$  (vCH) and 1480, 1431, 1312 cm<sup>-1</sup> (vring). NMR spectra of 1, recorded in dmso- $d_6$  solution, also indicated the coordination of thiourea and triphenylphosphine: <sup>1</sup>H NMR (ppm):  $\delta$  8.13 (s, -NH<sub>2</sub>),  $\delta$ 7.80 (s,  $-NH_2$ ),  $\delta$  7.63–7.46 (m, Ar–H),  $\delta$  2.48 (s,  $-CH_3$ ); <sup>13</sup>C{<sup>1</sup>H} (ppm):  $\delta$  206.9 (C=S),  $\delta$  134.2–128.4 (C<sub>Ar</sub>).  ${}^{31}P{}^{1}H{}$  NMR (ppm):  $\delta$  194.6. The presence of a CH<sub>3</sub>OH solvate was detected by the low-field <sup>1</sup>H NMR signal at  $\delta$ 9.75 (s, -OH). Regarding to the IR spectrum of 2, the coordination of the tmen ligand was detected by the disappearance of the band at  $2329 \text{ cm}^{-1}$ , attributed to vCN of [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] precursor and the presence of multiple bands centered at 3020-2850 cm<sup>-1</sup> (vCH<sub>3</sub> and vCH<sub>2</sub> vibrational modes) as well the absorptions found at 1468 (vCN) and 808 cm<sup>-1</sup> ( $\delta$ CH).

The ORTEP representation of the molecular structure of the asymmetric units for compound  $1 \cdot CH_3OH$  with the atom labeling schemes is presented in Fig. 1.

In compound  $1 \cdot CH_3OH$ , the palladium coordination geometry is approximately square planar formed by one sulfur (from tu), one phosphorus (from PPh<sub>3</sub>) and two *cis*-related chloro atoms. The Pd—Cl bond distance *trans* 



Fig. 1. ORTEP representation of the asymmetric unit with labeling scheme for  $1 \cdot CH_3OH$ . Key geometrical parameters: Pd—Cl1 2.3186(2) Å, Pd—Cl2 2.3801(1) Å, Pd—P 2.2440(1) Å, Pd—S 2.3191(1) Å, and Cl1—Pd—Cl2 88.94(6)°, Cl1—Pd—S 177.44(5)°, Cl1—Pd—P 93.24(5)°, S—Pd—P 84.30(5)°, Cl2—Pd—S 93.56(5)°, Cl2—Pd—P 175.12(6)°.

to the sulfur in  $[PdCl_2(PPh_3)(tu)]$  is 2.3186(2) Å, which is shorter by 0.0615 Å than the Pd—Cl one *trans* to phosphorus, clearly showing the *trans* influence of the thiourea and triphenylphosphine ligands. Methanol solvate molecules are linked with N1 atoms from thiourea ligands via hydrogen bonding interaction (N1...O1a 2.846(8) Å, H2...O1a 2.060 Å, N1—H2...O1a 154.00°).

The ORTEP perspective of the molecular structure of complex 2 with the atom numbering scheme is given in Fig. 2. The molecular structure of 2 revealed that the geometry around the Pd(II) is essentially square planar in which the metal atom is coordinated to two chloride anions and a neutral N, N, N', N'-tetramethylethylenediamine chelate.

In the past few years, much attention have been devoted to the hydrogen bonding involving metal-halides (M-X) since they can be successfully employed to assembly molecular building blocks into highly ordered transition metalbased supramolecular architectures owing their directional character. Metal-bound chlorides (M-Cl) are able to engage in hydrogen bonds with strong (i.e. N-H, O-H) and weak donors groups (i.e. C-H). According to Brammer et al. [3], C-H...Cl-M hydrogen bonds behave similarly to the stronger D-H...Cl-M (D = N, O) despite the fact that C-H...Cl-M interactions possess less directional preference.

In the crystal packing of 1, *cis*-coordinated chloride groups participate in hydrogen bonding of the N-H···Cl-Pd and C-H···Cl-Pd type. Two molecules of 1 are joined via N-H···Cl-Pd hydrogen bonds (N2···Cl1 3.382(6) Å, H2···Cl1 2.670 Å, N2-H2···Cl1 140.00°), involving one of the two Cl-Pd moieties and one NH<sub>2</sub> group from the thiourea ligand, giving rise to the formation of a  $R_2^2(12)$ dimer. The same Cl-Pd moiety also takes part in weak interaction C-H···Cl-Pd (C10···Cl1 3.590(7) Å, H10···Cl1 2.810 Å, C10-H10···Cl1



Fig. 2. ORTEP representation of the asymmetric unit with labeling scheme for **2**. Key geometrical parameters: Pd—Cl1 2.303(3) Å, Pd—Cl2 2.300(3) Å, Pd—N1 2.080(7) Å, Pd—N2 2.063(7) Å, and Cl1—Pd—Cl2 90.97(11)°, N1—Pd—N2 84.90(3)°, Cl1—Pd—N1 91.50(2)°, Cl1—Pd—N2 176.20(2)°, Cl2—Pd—N1 177.50(2)°, Cl2—Pd—N2 92.70(2)°.



Fig. 3. Packing view of the supramolecular ribbon formed by N-H···Cl-Pd and C-H···Cl-Pd interactions in 1.

143.00°) with a phenyl ring of a neighboring dimer. The C-H···Cl-Pd distance of 2.810 Å for 1 agrees well with the values found for the  $[PdCl_2(3-Xpy)_2]$  complexes (X = F, Cl, Br, I; py = pyridine) (2.783–2.864 Å) [9].

The cooperative effect of  $N-H\cdots Cl-Pd$  and  $C-H\cdots Cl-Pd$  intermolecular forces results in extended supramolecular chains (Fig. 3).

The crystal packing of **2** is determined by non-conventional C—H···Cl—Pd hydrogen bonds since other stronger interactions are absent (Fig. 4). Molecules of **2** self-assemble into one-dimensional infinite zig-zag ribbons through C—H···Cl—Pd hydrogen bonding involving one chloride acceptor from Cl—Pd moiety and one hydrogen atom from -CH<sub>3</sub> group of the N,N,N',N'-tetramethylethylenediamine ligand of an adjacent [PdCl<sub>2</sub>(tmen)] molecule (C2···Cl1 3.611(9) Å, H22···Cl1 2.820 Å, C2—H22···Cl1 140.00°). Methylene groups (-CH<sub>2</sub>-) from N,N,N',N'-tetramethylethylenediamine ligand do not participate in C—H···Cl interactions. Neighbouring 1D chains of **2** are assembled into a 2D layered structure through intermolecular C—H···Cl hydrogen bonds (C6···Cl2 3.747(8) Å, H62···Cl1 2.800 Å, C6—H62···Cl1 167.00°). Analysis of the crystal structure of **2** also reveals the presence of intramolecular C5—H51···Cl1 and C3—H31···Cl2 interactions, whose C···Cl separations are 3.320(9) and 3.239(11) Å with H···Cl distances of 2.760 and 2.690 Å, respectively. The C5—H51···Cl1 and C3—H31···Cl2 bond angles are 118.0° and 117.0(0)°, respectively. The C—H···Cl intermolecular H-bonds of 2.712 and 2.784 Å are also responsible for the formation of supramolecular sheets of [CoCl<sub>2</sub> (tmen)] [10].

In conclusion, the present study showed that the  $C-H\cdots Cl-Pd$  interactions play an important role in the self-assembly of *cis*-palladium complexes as building blocks. However, systematic investigations on such non-conventional hydrogen bonds in coordination compounds are necessary in order to explore their potential use as organizing elements in the rational construction of functional



Fig. 4. Packing view of 2D supramolecular sheet formed by C-H···Cl-Pd hydrogen bonds in 2.

transition metal-based supramolecules. Further investigation on the hydrogen-bonded metallosupramolecular species is still in progress in our laboratory.

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## Appendix A. Supplementary material

Additional materials, consisting of atomic coordinates and equivalent isotropic displacement parameters for nonhydrogen atoms, H-atom coordinates and isotropic displacement parameters, interatomic bond lengths and bond angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. CCDC 262005 (complex 1), and CCDC 262004 (complex 2). Copies of this information may be obtained free of charge from de Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; email:deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2006.02.012.

### References

- B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
  D. Braga, S.M. Draper, E. Champeil, F. Grepioni, J. Organomet. Chem. 573 (1999) 73;
   D. Braga, L. Maini, M. Polito, L. Scaccianoce, G. Cojazzi, F. Grepioni, Coord. Chem. Rev. 216–217 (2001) 225;
- D. Braga, F. Grepioni, Acc. Chem. Res. 33 (2000) 601.
- [2] G.R. Desiraju, Angew. Chem., Int. Ed. Engl. 34 (1995) 2311.
- [3] L. Brammer, E.A. Bruton, P. Sherwood, Cryst. Growth Des. 1 (2001) 277.
- [4] P.K. Thallypally, A. Nangia, Cryst. Eng. Comm. (2001) 27;
  S.L. James, G. Verspui, A.L. Spek, G. van Koten, Chem. Commun. (1996) 1309;
  - J.C.M. Rivas, L. Brammer, Inorg. Chem. 37 (1998) 4756.
- [5] A.V.G. Netto, R.C.G. Frem, A.E. Mauro, E.T. de Almeida, A.M. Santana, J. de Souza Jr., R.H.A. Santos, Inorg. Chim. Acta 350 (2003) 252.

[6] A.C. Moro, A.E. Mauro, S.R. Ananias, Eclet. Quím. 29 (2004) 57;
 A.V.G. Netto, R.C.G. Frem, A.E. Mauro, Polyhedron 24 (2005) 1086;

A.V.G. Netto, R.C.G. Frem, A.E. Mauro, Mol. Cryst. Liq. Cryst. 374 (2002) 255.

- [7] Compound  $1 \cdot CH_3OH$  was prepared by adding a mixture containing thiourea (30 mg; 0.39 mmol) and triphenvlphosphine (100 mg; 0.39 mmol) dissolved in 10 ml of CHCl<sub>3</sub>/CH<sub>3</sub>OH (1:1) to an orange suspension of [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (1) (100 mg; 0.39 mmol) in 10 ml of CHCl<sub>3</sub>. Slow evaporation of the yellow solution afforded orange crystals of good quality for X-ray diffraction studies. Yield 45 %. m.p. = 148 °C. Anal. Calc. for C<sub>20</sub>H<sub>23</sub>N<sub>2</sub>SOPCl<sub>2</sub>Pd: C, 43.80; H, 4.24; N, 5.12. Found: C, 43.70%; H, 4.04%; N, 5.38%. Compound 2: To a solution of [PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>] (1) (1.00 g; 3.85 mmol) in 10 ml of acetone, was added 0.58 mL of N, N, N', N'-tetramethylethylenediamine (tmen). The precipitation initialized immediately. After 30 min of stirring at room temperature, the suspension was filtered off and the yellow solid was washed with acetone and dried in vacuo Yield 85%. The filtrate was left to evaporate, yielding suitable single crystals for X-ray diffraction determination. m.p. = 218 °C. Anal. Calc. for C<sub>6</sub>H<sub>16</sub>N<sub>2</sub>Cl<sub>2</sub>Pd: C, 24.6; H, 5.51; N, 9.50. Found: C, 24.7%; H, 5.67%; N, 9.70 %.
- [8] Data were collected on a Enraf-Nonius CAD4 diffractometer. Crystallographic data for 1 CH<sub>3</sub>OH:  $M_{\rm w} = 547.76$ , triclinic, space group  $P\bar{1}$ , a = 9.8900(1) Å, b = 10.5556(1) Å, c = 12.9519(1) Å, Z = 2,  $\alpha = 99.370(1)^{\circ}, \ \beta = 111.223(1)^{\circ}, \ \gamma = 108.266(1)^{\circ}, \ V = 1137.1(2) \text{ Å}^3,$  $D_{\rm c} = 1.600 \text{ mg m}^{-3}, \mu = 1.227 \text{ mm}^{-1}, F(000) = 552$ , crystal dimension 0.10 · 0.15 · 0.15 mm, of 829 reflections collected, 799 were independent  $[R_{int} = 0.009]$  and used in all calculations. The R values are  $R_1 = 0.0182$  and  $wR_2 = 0.0542 [I > 2r(I)]$ ; max/min residual electron density: 0.47,  $-0.53 \text{ e/Å}^3$ . Crystallographic data for **2**:  $M_w = 293.53$ , monoclinic, space group Cc, a = 16.0805(1) Å, b = 6.023(1) Å, c = 11.916(1) Å, Z = 4,  $\alpha = 90^{\circ}$ ,  $\beta = 113.022(1)^{\circ}$ ,  $\gamma = 90^{\circ}$ , V = 1062.3(2) Å<sup>3</sup>,  $D_c = 1.835$  Mg.m<sup>-3</sup>,  $\mu = 2.197$  mm<sup>-1</sup>, F(000) = 584,  $K_{\alpha} = 0.71073 \text{ Å}, T = 293 \text{ K}, \text{ crystal dimension } 0.10 \cdot 0.10 \cdot 0.15 \text{ mm},$ of 1928 reflections collected, 1775 were independent [ $R_{int} = 0.024$ ] and used in all calculations. The R values are  $R_1 = 0.0283$  and  $wR_2 = 0.0650 [I > 2r(I)];$  max/min residual electron density: 0.39,  $-0.36 \text{ e/A}^3$ . The structure was solved using the WINGX system by SIR92 and refined using by full matrix least squares and difference Fourier methods. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, Summary of Data CCDC Nos. 262005/262004.
- [9] F. Zordan, L. Brammer, P. Sherwood, J. Am. Chem. Soc. 127 (2005) 5979.
- [10] A. Johansson, E. Wingstrand, M. Hakansson, Inorg. Chim. Acta 358 (2005) 3293.