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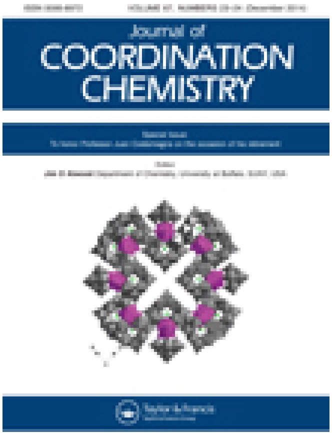

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Bis(oxamato)palladate(II) complexes: synthesis, crystal structure and application to catalytic Suzuki reaction

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Bis(oxamato)palladate(II) complexes: synthesis, crystal structure and application to catalytic Suzuki reaction

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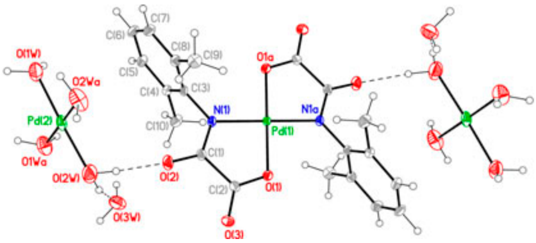

New bis(oxamato)palladate(II) complexes, $[Pd(H_2O)_4][Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$ (**1**), $(n\text{-}Bu_4N)_2[Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$ (**2a**), and $(n\text{-}Bu_4N)_2[Pd(2,6\text{-}Me_2pma)_2]\cdot 2CHCl_3$ (**2b**) (2,6-Me_2pma = *N*-2,6-dimethylphenyoxamate and $n\text{-}Bu_4N^+$ = tetra-*n*-butylammonium), have been synthesized and the structures of **1** and **2b** characterized by single-crystal X-ray diffraction. Complex **1** is a double salt constituted by tetraaquapalladium(II) cations and bis(oxamato)palladate(II) anions interlinked by hydrogen bonds. The palladium(II) ions in **1** are four-coordinate with two oxygens and two nitrogens from two fully deprotonated oxamate ligands (anion), and four water molecules (cation) building centrosymmetric square-planar surroundings. Centrosymmetric bis(oxamato)palladate(II) anions occur in **2b** as in **1**, the charge balance in this compound being ensured by the bulky $n\text{-}Bu_4N^+$. The catalytic role of **1** and **2a** for the Suzuki reaction has been investigated by using a series of aryl iodide/bromide derivatives in the conventional organic medium dimethylformamide. The tetraaquapalladium(II) unit in **1** appears to be active in the catalytic Suzuki cross-coupling reactions, but it readily decomposes to inactive palladium black.

Keywords: Palladium(II); Oxamate; Crystal structure; Double salt; Suzuki reaction

1. Introduction

N,N′-substituted oxamate or *N*-substituted oxamidate ligands form very stable complexes with copper(II) ions in aqueous solution [1]. Understanding the species formed in this

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*Corresponding authors. Email: donatella.armentano@unical.it (D. Armentano); miguel.julve@uv.es (M. Julve); salah.stiriba@uv.es (S.-E. Stiriba) medium has allowed the rational preparation of a great variety of homo and heterometallic species [2, 3]. This stability as well as the remarkable ability of oxamate and oxamidate to mediate magnetic interactions between paramagnetic metal ions bridged by them [4] accounts for their use in molecular magnetism being for instance at the origin of a rational approach to molecule-based magnets [5], the introduction of the concept of irregular spin state [6], and to the extension of the spin polarization mechanism to coordination compounds [7]. More recent efforts with specifically substituted oxamate ligands have been directed towards the achievement of molecule-based multifunctional magnetic materials [8], illustrative examples being the preparation and characterization of single ion magnets [9], single molecule magnets [10], chiral single-chain magnets [11], porous/luminescent magnets [12], magnetic sensors of small guest molecules [13], pH-controlled switches for reversible formation of emulsions [14], and chiral 3-D metal–organic polymers [15].

Very recently, diamagnetic square-planar oxamate-containing palladium(II) complexes have been found to exhibit cytotoxic activity against leukemia cells [16] and also to act as very stable and highly efficient catalysts in palladium-catalyzed Suzuki and Heck reactions using active and less reactive aryl halides [17]. These results give an added value to the coordination chemistry of the oxamate ligands from both biological and organic catalysis viewpoints.

In the context of our research program with oxamate complexes covering these interesting Pd(II) systems, we have isolated the complexes $[Pd(H_2O)_4][Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$ (**1**), $(n\text{-}Bu_4N)_2[Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$ (**2a**), and $(n\text{-}Bu_4\ N)_2[Pd(2,6\text{-}Me_2pma)_2]\cdot 2CHCl_3$ (**2b**) ($2,6\text{-}Me_2pma$ = *N*-2,6-dimethylphenyoxamate). Their preparation, spectroscopic and structural characterization, and the study of their catalytic activity in the palladium-catalyzed Suzuki cross-coupling reaction of aryl halides and phenylboronic acid are subject of the present work.

2. Experimental

2.1. *Materials and methods*

NMR spectra (^1H and ^{13}C) were recorded on an Avance DRX 300 Bruker instrument at room temperature and referenced to residual protons in the solvent (^1H) or the solvent ^{13}C signal (^{13}C). Elemental analyses (C, H, and N) were carried out on a EuroEA3000 analyzer by the Servei Central d'Instrumentació Científica at the University of Jaume I. FTIR spectra (4000–450 cm^{-1}) were recorded with a Nicolet 5700 FTIR instrument. GC–MS spectra were performed with an Agilent 5973N mass spectrometer equipped with capillary columns (split/splitless, pulsed split, and pulsed splitless) at the Servicio Central de Soporte a la Investigación Experimental of the University of Valencia. The SEM-Edax microscopy analysis was performed on a Philips mod. XL 30 ESEM with microanalysis EDAX mod. PV 9760 and HOT STAGE to 1000 °C.

2.2. *Synthesis of the N-2,6-dimethylphenyloxamate proligand (EtH-2,6-Me₂pma)*

The ethyl ester derivative of *N*-2,6-dimethylphenyloxamic acid was prepared using the following synthetic procedure: 2,6-dimethylphenylaniline (83 mM) was dissolved in THF (250 mL), under a dinitrogen atmosphere in a two-necked round flask equipped with a condenser and subsequently treated with ethyl chlorooxoacetate (9.3 mL, 83 mM) in the presence of triethylamine (12 mL, 83 mM), at room temperature under continuous stirring for 30 min. The resulting solution was filtered and the solvent was removed under vacuum to afford an oily colorless crude, which quickly becomes solid. The white solid was suspended into water and filtered off, then washed with a small amount of diethyl ether, and dried under vacuum. Yield: 96%. IR (KBr/cm^{-1}): 3244 (N–H), 3027, 2977, 2923 (C–H), 1727, 1677 (C=O). ^{1}H NMR ($CDCl_3$) δ(ppm): 1.42–1.45 (t, 3H, CH_3), 2.25 (s, 6H, CH_3), 4.42–4.46 (q, 2H, CH_2), 7.11–7.13 (m, 3H, $H_{aromatic}$), 8.46 (s, 1H, NH); ^{13}C NMR ($CDCl_3$) δ(ppm): 14.4, 18.8, 64.0, 128.3, 128.6, 132.5, 135.4, 155, 161.3. Anal. Calcd for $C_{12}H_{15}NO_3$ (221 g M^{-1}): C, 65.14; H, 6.83; N, 6.33. Found: C, 65.31; H, 6.73; N, 6.40%.

2.3. *Synthesis of $[Pd(H_2O)_4][Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$ (1)*

An aqueous solution of KOH (15 mL, 1.2 mM) was poured into a two-necked flask containing suspension of the EtH-*N*-2,6-Me_2pma proligand (0.6 mM) in 10 mL of CH_3CN. Then, an aqueous solution of $K_2[PdCl_4]$ (0.2 g, 0.6 mM) was added dropwise under continuous stirring and the mixture was heated at 60 °C overnight. The resulting yellow solution afforded yellow parallelepipeds within 2–3 days, upon very slow evaporation at room temperature. Yield: 88%. IR (KBr/cm^{-1}): 3423 3327, 3246, 3155 (O–H), 2911 (C–H), 1670, 1638, 1630, 1577 (C=O). Anal. Calcd for $C_{20}H_{30}N_2O_{12}Pd_2$ (**1**, 702 g M^{-1}): C, 34.16; H, 4.30; N, 3.98. Found: C, 34.01; H, 4.22; N, 4.05%.

2.4. *Synthesis of $(n\text{-}Bu_4N)_2[Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$ (2a) and $(n\text{-}Bu_4N)_2[Pd(2,6\text{-}Me_2pma)_2]\cdot 2CH_2Cl_3$ (2b)*

A methanolic solution of 1.0 M *n*-Bu_4NOH (1.5 mL, 1.2 mM) was added directly to a suspension of the proligand (0.6 mM, 10 mL of CH_3CN) in a two-neck round flask under continuous stirring. Then, an aqueous solution of K_2PdCl_4 (0.1, 0.30 mM) was added dropwise to the resulting solution and the reaction mixture was heated at 60 °C for 10 h. The resulting mixture was filtered and the volume reduced under vacuum. The remaining concentrated solution was treated three times with dichloromethane to extract the complex from the aqueous solution. The addition of *n*-hexane to the dichloromethane solution afforded **2a**, a pale yellow powder which was collected by fltration and dried in the open air. Yield: 89%. X-ray quality yellow prisms of **2b** were grown by slow recystallization of **2a** in a chloroform/*n*-hexane mixture. The formula of **2b** was determined by X-ray diffraction on single cystals. Spectroscopic data for **2a** are given as follows: IR (KBr/cm^{-1}): 3433 (O–H), 2961, 2936, 2873 (C–H), 1670, 1638, 1604, 1582 (C=O). ^{1}H NMR (DMSO-d_6) δ(ppm): 0.90–0.94 (t, 12H, *n*-Bu_4N^+), 1.30–1.32 (m, 16H, TBA), 1.55–1.58 (m, 16H, *n*-Bu_4N^+), 2.24 (s, 24H, CH_3), 3.13–3.16 (m, 16H, TBA), 6.80–6.87 (m, 6H, $H_{aromatic}$). Anal. Calcd for $C_{52}H_{94}N_4O_8Pd$ (**2a**, 1008 g M^{-1}): C, 61.85; H, 9.38; N, 5.55. Found: C, 62.05; H, 9.19; N, 5.48%.

2.5. *General procedure for the Suzuki reaction*

A test tube with screw cap and valve was charged with a magnetic stir bar, the pre-catalyst (**1** or **2a**; 1 M% Pd with respect to the aryl halide), the aryl halide (0.50 mM), Et_3N (1.00 mM), the aryl boronic acid (0.75 mM), and dimethylformamide (DMF) (4 mL). The mixture was heated under continuous stirring at 80 °C in the open air. The reaction was monitored using liquid chromatography on silica gel. The reaction mixture was cooled, diluted with water (3 mL), and extracted three times (3 × 5 mL) with *n*-pentane. The extracts were combined and dried over magnesium(II) sulfate. The yield was determined by GC–MS analysis using perfluorotributylamine (PFTBA).

2.6. *X-ray crystallography*

Single-crystal X-ray diffraction data for 1 and 2b were collected at 296 K on a Bruker-Nonius X8-APEXII CCD area detector system using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and processed through the SAINT [18] reduction and SADABS [19] absorption software. Due to the poor crystal quality, a lower θ_{max} of diffraction was obtained for 2b, even if all possible steps were undertaken to ensure that the experiment was able to extract the best diffracting power from the sample. However, since the solution and refinement parameters are reasonable, we are confident that the crystal structure found is consistent. The structures were solved by direct methods and subsequently completed by Fourier recycling using SHELXTL-2013 [20] software package, then refined by full-matrix least-squares refinements based on F^2 with all observed reflections. All non-hydrogen atoms were refined anisotropically in the case of 1, while they were refined isotropically for 2b in order to reduce the number of parameters. The hydrogens from the 2,6-dimethylphenyl substituent on the oxamate (1 and 2b) and those from the tetra-*n*-butylammonium cations and chloroform lattice molecules (2b) were included at geometrically calculated positions and refined using a riding

Table 1. Crystallographic data and structure refinement for **1** and **2**b.

Compound	**1**	**2b**
Empirical formula	$C_{20}H_{30}N_2O_{12}Pd_2$	$C_{54}H_{92}Cl_6N_4O_6Pd_1$
Formula weight	703.26	1212.42
Temperature	296(2) K	296(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	$P2_1/n$
Unit cell dimensions	a = 22.620(2) Å	a = 11.940(4) Å
	b = 7.7498(7) Å	b = 18.197(7) Å
	c = 15.5036(15) Å	c = 14.892(5) Å
β	108.005(7)°	92.922(10)°
Volume	2584.7(4) Å^3	3231(2) Å^3
Z	4	2
Density (calculated)	1.807 Mg m^{-3}	1.246 Mg m^{-3}
Absorption coefficient	1.454 mm^{-1}	0.580 mm^{-1}
F (0 0 0)	1408	1268
Crystal size	0.08 × 0.12 × 0.10 mm^3	0.04 × 0.08 × 0.06 mm^3
Theta range for data collection	1.893–27.000°	2.134–12.995°
Reflections collected	21312	10301
Independent reflections	2820 [R(int) = 0.0252]	846 [R(int) = 0.0633]
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2820/9/185	846/0/136
Final R indices [$I > 2\sigma(I)$]	[a]R_1 = 0.0449, [b]wR_2 = 0.0929	R_1 = 0.0799, wR_2 = 0.2094
R indices (all data)	R_1 = 0.0519, wR_2 = 0.0977	R_1 = 0.0841, wR_2 = 0.2128
[c]Goodness-of-fit on F^2	1.108	1.185
Largest diff. peak and hole	3.137 and −2.201 e Å^{-3}	0.434 and −0.312 e Å^{-3}

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.
[c] $S = [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

model. The hydrogens on water molecules in 1 were located on the ΔF map and refined with restraints on O–H distances and H–O–H angles. The high residual maxima and minima in the final Fourier difference maps in 1 (3.137 and −2.201 e Å^{-3}, respectively) were near Pd(2). Crystal data and refinement conditions (1 and 2b), selected bond lengths (1 and 2b) bond angles (1 and 2b) and hydrogen bonds (1) are listed in tables 1–4.

Table 2. Selected bond lengths (Å) for **1** and **2b**.

Compound **1**			
Pd(1)–O(1)	2.020(3)	C(1)–C(2)	1.546(6)
Pd(1)–N(1)	2.023(3)	C(3)–C(4)	1.402(6)
Pd(2)–O(2W)	2.045(5)	C(3)–C(8)	1.405(5)
Pd(2)–O(1W)	2.051(5)	C(4)–C(5)	1.401(6)
O(1)–C(2)	1.291(5)	C(4)–C(10)	1.519(6)
O(2)–C(1)	1.258(5)	C(5)–C(6)	1.389(7)
O(3)–C(2)	1.237(5)	C(6)–C(7)	1.389(7)
N(1)–C(1)	1.329(5)	C(7)–C(8)	1.409(6)
N(1)–C(3)	1.439(5)	C(8)–C(9)	1.511(6)
Compound **2b**			
Pd(1)–O(1)	1.97(2)	N(1)–C(2)	1.29(3)
Pd(1)–N(1)	2.03(2)	N(1)–C(3)	1.42(2)
O(3)–C(2)	1.23(3)	C(1)–C(2)	1.62(4)
O(2)–C(1)	1.20(4)	C(4)–C(10)	1.52(3)
O(1)–C(1)	1.25(4)	C(8)–C(9)	1.49(3)

Table 3. Selected bond angles (°) for **1** and **2b**.*[&]

Compound **1**			
O(1)–Pd(1)–O(1a)	180.0(1)	O(3)–C(2)–C(1)	119.1(4)
O(1)–Pd(1)–N(1a)	98.4(1)	O(1)–C(2)–C(1)	116.8(3)
O(1)–Pd(1)–N(1)	81.6(1)	C(4)–C(3)–C(8)	121.9(4)
N(1a)–Pd(1)–N(1)	180.0	C(4)–C(3)–N(1)	117.4(3)
O(2Wb)–Pd(2)–O(1W)	91.5(3)	C(6)–C(5)–C(4)	120.7(4)
O(2W)–Pd(2)–O(1W)	177.3(2)	C(5)–C(6)–C(7)	119.8(4)
O(1Wb)–Pd(2)–O(1W)	88.6(3)	C(6)–C(7)–C(8)	121.6(4)
C(2)–O(1)–Pd(1)	114.0(2)	C(8)–C(3)–N(1)	120.7(4)
C(1)–N(1)–Pd(1)	114.9(3)	C(5)–C(4)–C(10)	121.1(4)
C(3)–N(1)–Pd(1)	123.7(2)	C(3)–C(4)–C(10)	120.2(4)
C(1)–N(1)–C(3)	121.2(3)	C(5)–C(4)–C(3)	118.7(4)
O(2)–C(1)–N(1)	127.6(4)	C(3)–C(8)–C(7)	117.4(4)
O(2)–C(1)–C(2)	119.8(4)	C(3)–C(8)–C(9)	121.3(4)
N(1)–C(1)–C(2)	112.5(3)	C(7)–C(8)–C(9)	121.3(4)
O(3)–C(2)–O(1)	124.1(4)		
Compound **2b**			
O(1)–Pd(1)–O(1a)	180.0(11)	O(3)–C(2)–N(1)	129(4)
O(1)–Pd(1)–N(1)	80.7(9)	O(3)–C(2)–C(1)	120(4)
O(1)–Pd(1)–N(1a)	99.3(9)	N(1)–C(2)–C(1)	111(4)
C(1)–O(1)–Pd(1)	118(3)	C(4)–C(3)–N(1)	119(2)
C(2)–N(1)–C(3)	122(3)	C(8)–C(3)–N(1)	121(2)
C(2)–N(1)–Pd(1)	116(3)	C(3)–C(4)–C(10)	121(2)
C(3)–N(1)–Pd(1)	121.9(18)	C(5)–C(4)–C(10)	119(2)
O(2)–C(1)–O(1)	132(4)	C(7)–C(8)–C(9)	121(2)
O(2)–C(1)–C(2)	114(4)	C(3)–C(8)–C(9)	119(2)
O(1)–C(1)–C(2)	114(4)		

*Symmetry transformations used to generate equivalent atoms: (a) $-x + 3/2$, $-y + 7/2$, $-z + 1$. (b) $-x + 1$, y, $-z + 1/2$.

[&] Symmetry transformations used to generate equivalent atoms: (a) $-x + 1$, $-y + 2$, $-z$.

Table 4. Hydrogen bonds for 1.*

D–H···A	d(D–H), Å	d(H···A), Å	d(D···A), Å	<(D–H···A), °
O(1W)–H(1W1)···O(2c)	0.96(3)	2.31(4)	3.095(6)	139(4)
O(1W)–H(1W1)···O(3c)	0.96(3)	2.24(3)	3.083(6)	146(4)
O(2W)–H(2W2)···O(2)	0.99(3)	1.97(3)	2.958(7)	175(4)
O(3W)–H(3W1)···O(3)	0.95(3)	2.17(4)	3.005(6)	146(5)
O(3W)–H(3W2)···O(3d)	0.96(3)	2.02(3)	2.945(6)	163(5)

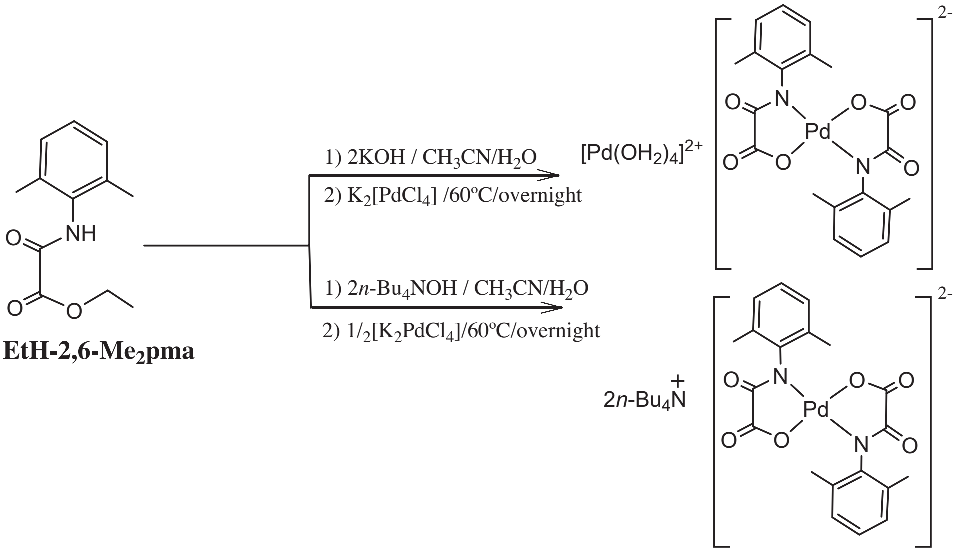
*Symmetry transformations used to generate equivalent atoms: (c) $-x + 1, y - 1, -z + 1/2$; (d) $-x + 1, -y + 4, -z + 1$.

3. Results and discussion

3.1. *Syntheses and spectroscopic characterization*

The preparations of **1** and **2a** were done by following the same synthetic methodology that has been employed for other mononuclear bis(oxamato)palladate(II) species [17]. So, the reaction of $K_2[PdCl_4]$ with the *N*-2,6-dimethylphenyloxamate dianion [produced *in situ* by the treatment of its monoester derivative with potassium hydroxide (Pd : oxamate proligand : OH^- 1 : 1 : 2 molar ratio) in a mixture of water/acetonitrile (1.5:1, v/v)] at 60 °C overnight led to the formation of a yellow solution that was allowed to slowly evaporate at room temperature. Crystals of the double salt $[Pd(H_2O)_4][Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$ (**1**) were grown within a couple of days (see scheme 1).

The use of $n\text{-}Bu_4NOH$ as base (Pd : oxamate proligand : OH^- 1 : 2 : 4 molar ratio) led to the formation of the usual anionic bis(oxamato)palladium(II) with the tetra-*n*-butylammonium countercation (**2a**). This compound was prepared for comparative purposes of the reaction conditions as shown in scheme 1. The reaction in water afforded, as previously reported, the supramolecular complex $\{K_4(H_2O)_3]cis\text{-}[Pd^{II}(2,6\text{-}Me_2pma)_2]_2\}_n$ [17(b)]. Consequently, it appears that the nature of the cation from the base and the solvent of the



Scheme 1. Synthetic route for **1** and **2a**.

reaction strongly affects the formation, stability, and structural features of the oxamate-containing palladium(II) compounds.

The high-frequency region of the IR spectrum of **1** exhibits a strong band at 3422 cm^{-1} due to O–H stretch together with the characteristic C–H vibrations (2961, 2933 and 2873 cm^{-1}) of the phenyl ring of the *N*-2,6-dimethylphenyloxamate ligand. Additionally, two strong absorptions are at 1616 and 1641 cm^{-1} which are attributed to C=O vibrations, supporting the coordination of the 2,6-Me_2pma dianion to palladium(II). Identical peaks concerning the aromatic C–H and C=O stretching vibrations are observed in the IR spectrum of **2a**, supporting also the occurrence of coordinated 2,6-Me_2pma. ^{1}H NMR experiments support the formation of the 2,6-Me_2pma dianion, as indicated by the disappearance of the peaks of both ethyl and NH groups of the proligand, and its coordination to palladium(II) to yield **2a** with n-Bu_4N^+ as countercation. These spectroscopic features have been confirmed by X-ray diffraction on single crystals (*vide infra*).

3.2. *Crystal structures of [Pd(H_2O)$_4$][Pd(2,6-Me_2pma)$_2$]·2H_2O (1) and (n-Bu_4 N)$_2$[Pd (2,6-Me_2pma)$_2$]·2$CHCl_3$ (2b)*

Compounds 1 and 2b crystallize in the monoclinic space groups *C2/c* and $P2_1/n$, respectively, with half a molecule in the asymmetric unit, the second half being generated by the crystallographic inversion center. Each structure consists of *trans*-[Pd(2,6-Me_2pma)$_2$]$^{2-}$ and [Pd(H_2O)$_4$]$^{2+}$ (1) or n-Bu_4 N^+ (2b) counterions plus crystallization water (1) and chloroform (2b) (figures 1 and 2). Anions and cations in 1 are assembled by an extended network of hydrogen bonds into a 3-D supramolecular structure (figure 3), while the bis(oxamate)palladate(II) species in 2b are well separated by the bulky n-Bu_4N^+ cations.

The structures of **1** and **2b** have in common the presence of the *trans*-[Pd(2,6-Me_2pma]$^{2-}$ mononuclear unit where the palladium(II) ion is four-coordinate with two amidate nitrogens [N(1) and N(1a)] and two carboxylate oxygens [O(1) and O(1a)], building a slightly distorted square-planar coordination. The reduced bite angle of the chelating oxamate [81.6(1)° (**1**) and 80.9(9)° (**2b**)] accounts for deviations from the ideal geometry; in fact, the Pd(II) and the atoms building its surrounding lie exactly on a plane for symmetry reasons. The Pd–N/Pd–O

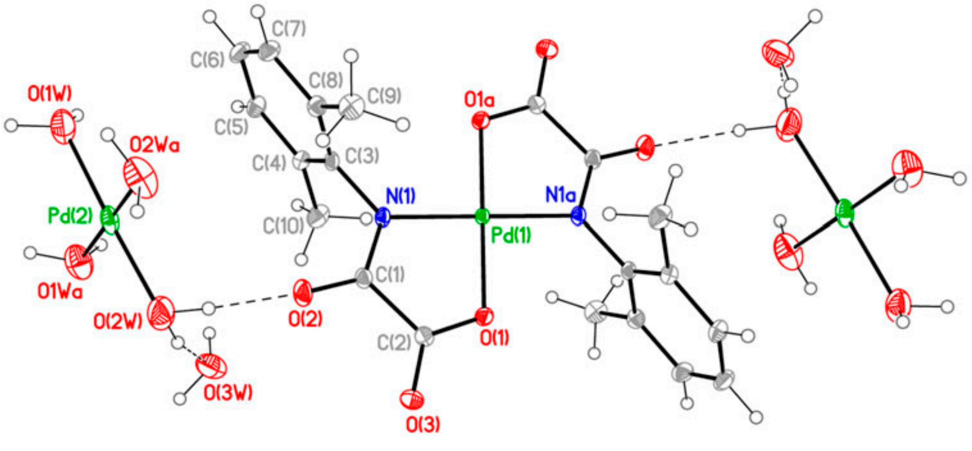


Figure 1. ORTEP drawing of the anionic complex structure of 1 showing the atom numbering scheme and the hydrogen bonds (broken lines) interconnecting the oxamate and *aqua* ligands.

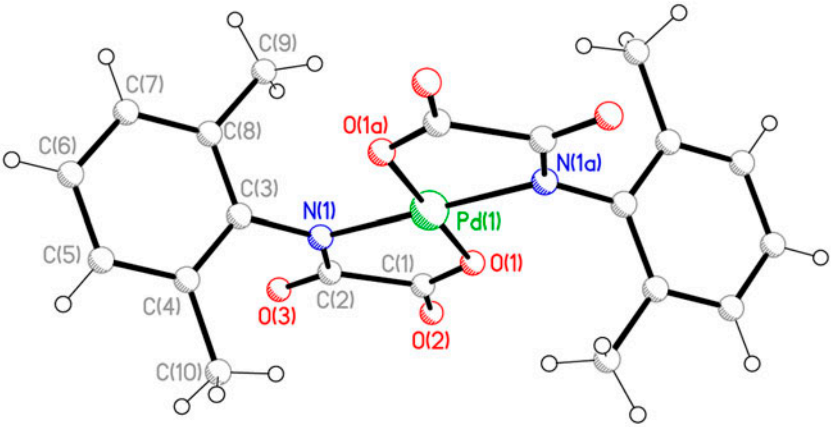


Figure 2. Perspective view of the anionic complex structure of **2b** showing the atom numbering scheme.

bond lengths of 2.023(3)/2.04(2) (**1**) and 2.020(3)/1.97(2) Å (**2b**) compare well with those found in the oxamato-containing palladium(II) complexes $\{[\mathrm{Na(H_2O)}]_2$*trans*-$[\mathrm{Pd^{II}}(2,6\text{-}\mathrm{Me_2pma})_2]\}_n$, $(n\text{-}\mathrm{Bu_4N})_2$*trans*-$[\mathrm{Pd(2\text{-}Mepma)_2}]\cdot 4\mathrm{H_2O}$ [2-Mepma = *N*-2-methylphenyloxamate], $(n\text{-}\mathrm{Bu_4N})_2$*trans*-$[\mathrm{Pd(4\text{-}Mepma)_2}]\cdot 4\mathrm{H_2O}$ [4-Mepma = *N*-4-methylphenyloxamate], $\mathrm{Na[Pd(Hpba)]\cdot 2H_2O}$ [$\mathrm{H_4pba}$ = 1,3-propylenebis(oxamic acid)], and $\mathrm{K_2[Pd(opba)]\cdot 2H_2O}$ [$\mathrm{H_4opba}$ = *N,N′*-1,2-phenylenebis(oxamic acid)] [average Pd–N/Pd–O distances of 2.020(1)/2.009(1), 2.021(1)/2.038(1), 2.021(1)/2.021(1), 1.970/2.040, and 1.928/2.055 Å, respectively] [17, 21, 22].

The plane at the Pd(II) ion and the mean plane of the oxamate group are almost coplanar [the values of the dihedral angle between these two planes (φ) are 2.20(4) (**1**) and 1.3(4)° (**2b**)]. Focusing on the phenyloxamate ligand, the dihedral angle between the 2,6-substituted phenyl ring and the mean plane of the oxamate group (ϕ) are 81.52(3) (**1**) and 80.0(4)° (**2b**), much closer to orthogonality than those observed in $\{[\mathrm{Na(H_2O)}]_2$*trans*-$[\mathrm{Pd^{II}}(2,6\text{-}\mathrm{Me_2pma})_2]\}_n$, $(n\text{-}\mathrm{Bu_4N})_2$*trans*-$[\mathrm{Pd(2\text{-}Mepma)_2}]\cdot 4\mathrm{H_2O}$, and $(n\text{-}\mathrm{Bu_4N})_2$*trans*-$[\mathrm{Pd(4\text{-}Mepma)_2}]\cdot 4\mathrm{H_2O}$ [$\phi = 75.79(4)$, 51.1(1), and 52.2(1)°, respectively] [17].

A tetraaquapalladium(II) cation is present in **1**, reminiscent of the situation found in the double salt $\mathrm{[Pd(NH_3]_4[Pd(opba)]}$ where the tetramminepalladium(II) is a counterion of the oxamato dianion $\mathrm{[Pd(opba)]^{2-}}$ [16]. The palladium(II) ion in this tetraaqua complex is also four-coordinate in a slightly distorted O(1w)O(2w)O(1wa)O(2wa) square-planar geometry. The values of the O(1w)–Pd(2)–O(2w), O(1w)–Pd(2)–O(1wa), and O(1w)–Pd(2)–O(2wa) bond angles are 177.3(2), 88.6(3), and 91.5(3)°, respectively, and the average $\mathrm{Pd{-}O_w}$ length is 2.048(5) Å.

Focusing on the crystal packing of **1**, hydrogen bond interactions involving coordinated and crystallization waters give layers of h*yper*-hydrated Pd(2) ions extending on the crystallographic *bc* plane (figure 3). The outer oxamate oxygens [O(2) and O(3)] of the anionic complex are anchored to these sheets through further hydrogen bonds, leading to an overall supramolecular 3-D motif (see table 4). The values of the shortest interionic metal–metal separations are 7.750(3) and 6.922(3) [Pd(1)···Pd(1e) and Pd(2)···Pd(1e) Å, respectively; symmetry code: (e) = x, $-y+1$, z].

The oxamate complex anions in the crystal packing of **2b** are well separated from each other most likely because of the presence of bulky $n\text{-}\mathrm{Bu_4N^+}$ cations; the shortest intermetallic

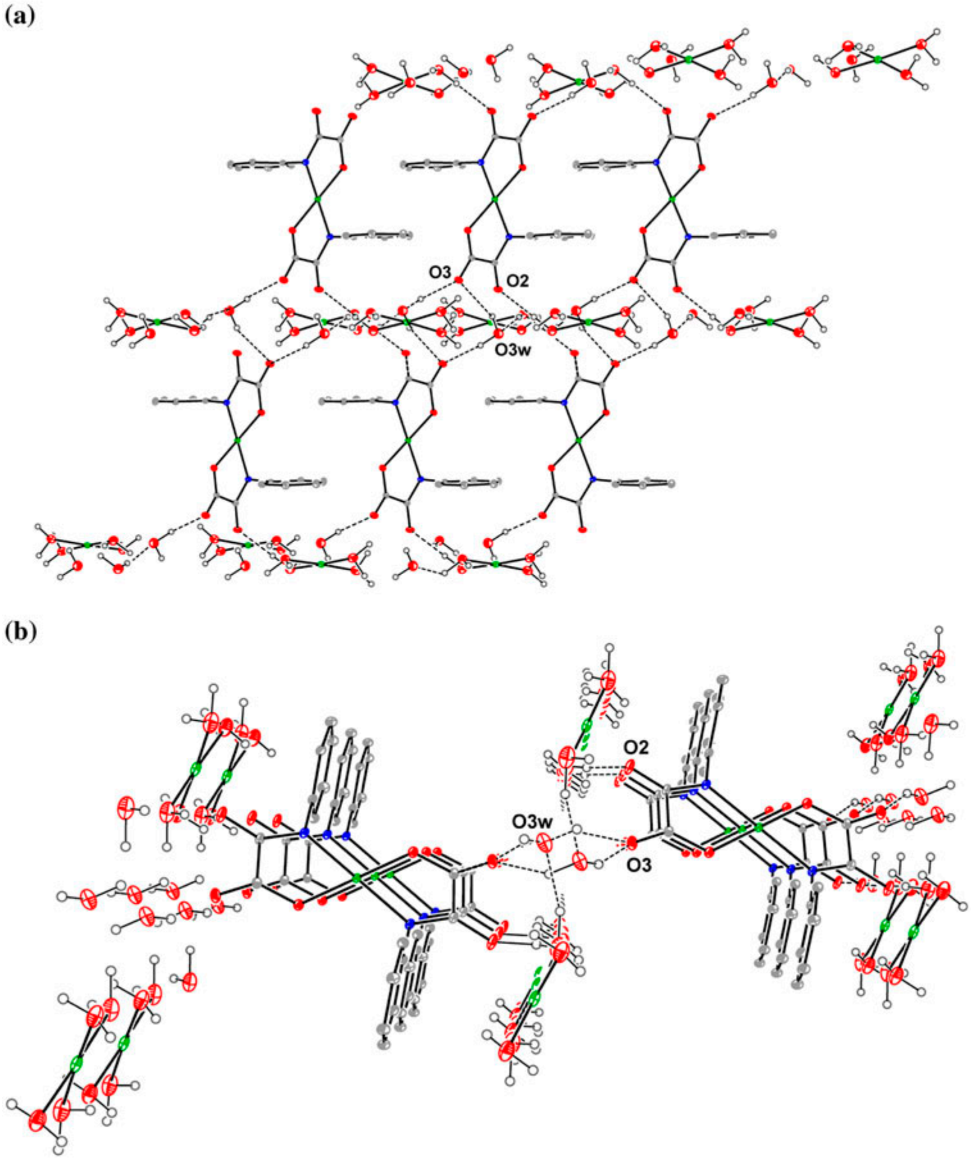


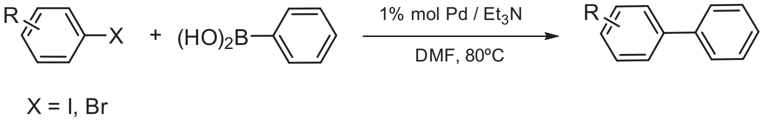
Figure 3. (a) View along the crystallographic *c* and (b) *b* axes of fragments of the crystal packing in **1**.

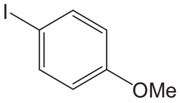
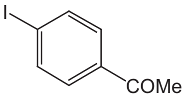
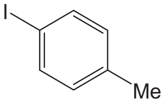
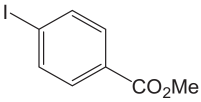
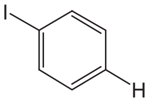
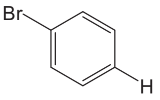
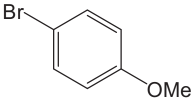
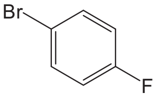
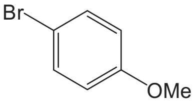
Pd(1)···Pd(1b) separation is 11.94(3) Å [symmetry code: (b)=−*x*, *y*, *z*] (figure S1, see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.975697). Chloroform crystallization molecules are intercalated in the free voids by weak Cl···H–C interactions.

3.3. *Catalytic studies*

Palladium complexes are widely used as catalysts for carbon–carbon bond-forming reactions [23]. These reactions are key steps in many syntheses of organic chemicals, natural products, as well as in a variety of industrial processes [24]. A successful example of this type of catalysis is the Suzuki cross-coupling reaction that works reliably, tolerating most functional groups both on the substrate and the products [25]. The catalytic activity of **1** has been tested in the Suzuki cross-coupling of phenylboronic acid as the standard boronic acid substrate and different aryl halides as the coupling partners (see table 5). The catalytic activity of **1** was compared to that of **2a**. With the new double salt **1** composed of anionic bis(oxamato) palladate(II) and cationic tetraaquapalladate(II) entities (1 M% Pd, 0.00025 mM of **1**),

Table 5. Suzuki cross-coupling reaction of aryl halides phenylboronic acid.[a]



Entry	Aryl halide	Time	Yield of biphenyl product (%) (catalyst used)[b]	
1		3 h	30 (**1**)	35 (**2a**)
2		3 h	55 (**1**)	56(**2a**)
3		18 h	28 (**1**)	30 (**2a**)
4		18 h	39 (**1**)	48 (**2a**)
5		30 min	50 (**1**)	60 (**2a**)
6		30 min	23(**1**)	26 (**2**)
7		30 min	17 (**1**)	28 (**2a**)
8		30 min	35 (**1**)	30 (**2a**)
9		3 h	29 (**1**)	29 (**2a**)

[a]Reaction conditions: aryl halide (1.0 mM), $PhB(OH)_2$ (1.2 mM), Et_3N (2.0 mM), 1% M of catalyst relative to arylhalide, DMF (3 mL), $T = 80$ °C.
[b]Determined by GC–MS spectroscopy using PFTBA as internal standard.

the use of 1.0 equivalent of aryl halide, 1.2 equivalents phenylboronic acid and 2.0 equivalents Et_3N as base in DMF at 80 °C results in moderate yields of the symmetrical and unsymmetrical biaryl products (17–55%), employing the less reactive bromo aryls and the very reactive iodo aryls. Applying the same catalytic conditions, bis(oxamato) palladated(II) complex **2a** featuring one palladium metal center *per* molecule was tested (1 M% Pd, 0.005 mM of **2a**), resulting in approximately the same moderate yields (25–60%) like **1**. The catalytic activity observed for **2a** featuring a discrete structure is lower compared to the activity shown by the same complex assembled through univalent alkaline counterions such as Na^+, K^+, Cs^+, and Rb^+. This is likely due to the bulky n-Bu_4N^+ present in **2a** [17(b)]. The values of the yield of the catalytic biaryl products obtained by using the new double salt **1** were found to be similar or slightly lower than those obtained with the mononuclear complex $(n\text{-}Bu_4N)_2[Pd(2,6\text{-}Me_2pma)_2]\cdot 2H_2O$ (**2a**). The same value of TON considering % M of PdII (twice in 1 than in 2b) in both reactions indicates that the PdII entities are equally activated because the identical number of mM of PdII were used for 1 and 2b. However, ready decomposition of the tetraaquapalladium(II) unit in 1 to metal palladium black occurs leading to inactive catalytic species at high temperatures.

4. Conclusion

A double salt composed of the anionic bis(*N*-2,6-dimethylphenyloxamato)palladate(II) and cationic tetraaquapalladium(II), assembled by water as ancillary group, has been obtained. bis(*N*-2,6-dimethylphenyloxamato)palladate(II) mononuclear species was also prepared featured by the organic cation tetra-*n*-butylammonium. Both compounds were easily prepared by control of the mixture of reaction solvents. Both catalyze the Suzuki cross-coupling of aryl halides and phenylboronic acid into biaryl products in moderate yields. The presence of the tetraaquapalladium(II) unit in a palladium(II) catalyst appears to readily decompose to palladium(0) black, a feature that shows the relevance of the coordinating ligand or protecting shell for the formation of active and stable palladium species during the catalytic cycle of palladium-catalyzed carbon–carbon coupling reactions.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center; CCDC reference numbers are 1024052 (**1**) and 1024053 (**2**). Copies of this information may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article: Crystal packing of **2** (figure S1).

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