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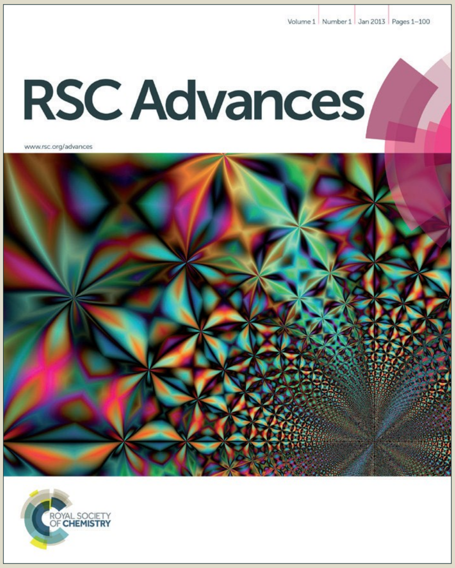

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Journal Name

ARTICLE

Intermolecular interactions in dictating the self-assembly of halogen derivatives of bis-(*N*-substituted oxamato)palladate(II) complexes†‡

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Three palladium(II) complexes of formula $(n\text{-Bu}_4\text{N})_2[\text{Pd(4-Fpma)}_2]$ (**1**), $(n\text{-Bu}_4\text{N})_2[\text{Pd(4-Clpma)}_2]\cdot 4\text{H}_2\text{O}$ (**2**) and $(n\text{-Bu}_4\text{N})_2[\text{Pd(4-Brpma)}_2]\cdot 4\text{H}_2\text{O}$ (**3**) [$n\text{-Bu4N}^+$ = tetra-*n*-butylammonium cation, 4-Fpma = *N*-4-fluorophenyloxamate, 4-Clpma = *N*-4-chlorophenyloxamate and 4-Brpma = *N*-4-bromophenyloxamate] have been prepared and their structures determined by single crystal X-ray diffraction. Each palladium(II) ion in **1**-**3** is four-coordinate with two oxygen and two nitrogen atoms from two fully deprotonated oxamate ligands building PdO_2N_2 square planar surroundings, the oxamate ligands exhibiting *trans* (**1** and **2**) and *cis* (**3**) dispositions. The fluoro substituent and the organic counterion in **1** are involved in C-H···F type interactions whereas the anionic complex assembly is drived by $\text{C-H}\cdots\text{O}_{\text{oxamate}}$ interactions. The structures of **2** and **3** shed light on the effects of the different chemical nature of chloro and bromo substituents on the C-H···X interactions joined to hydrogen bonds involving oxamate oxygen atoms and crystallization water molecules. The complex anions in **2** are interlinked by water chains to afford a supramolecular two-dimensional network where $\text{O}_\text{w}\cdots\text{O}_\text{w}$, $\text{O}_\text{w}\cdots\text{O}_{\text{oxamate}}$ and $\text{O}_\text{w}\cdots\text{Cl}$ hydrogen bonds are involved. The reduction of the polarity of C-Br bonds respect to C-X (X = F, Cl) is very likely to be one of the key reasons allowing for the *cis*-arrangement of the two 4-Brpma ligands around each palladium(II) ion of the anionic complex in **3** in water. These units are interconnected by hydrogen bonds between the peripheral oxamato-oxygens and a four-membered ring of water molecule leading to supramolecular cationic chains extending along the crystallographic *a* axis.

Introduction

Since the late 1990s, it was evident that other intermolecular forces than hydrogen bonds, namely halogen atom interactions could be used as robust design elements in crystal engineering.[1-8] Although the understanding of the competitiveness and/or cooperativeness between such intermolecular forces to assemble molecules in both chemistry and biology is still not well-understood, a structural competition between halogen and hydrogen bonds[9,10] has recently been detected, pointing out the great difficulty to define the hierarchy of these two intermolecular interactions whose strength and directionality are comparable.[2] Besides creating fundamental advances in understanding such forces in driving the formation of complex architectures, the main interest in such studies relies on the evidence that the properties of a given material deeply depend on the arrangement of either organic or inorganic entities in the solid state.[11]

Supramolecular motifs that can be achieved by the arrangement of mononuclear complexes as building units *via* intermolecular forces (hydrogen bonds and stacking interactions, for instance) have experienced a rapid growth during the last decades. This increasing interest has been driven by the large variety of supramolecular assemblies and molecular architectures with desired properties that can be achieved based on such directing intermolecular forces, contributing to the development of the crystal engineering.[12-25] A careful choice of the ligands, metal centres, spacers and reaction conditions are required in order to gain specific control over the topology of the resulting frameworks.[18-19]

Herein, we report on the supramolecular features on three non-isostructural compounds of formula $(n\text{-Bu}_4\text{N})_2[\text{Pd(4-Fpma)}_2]$ (**1**), $(n\text{-Bu}_4\text{N})_2[\text{Pd(4-Clpma)}_2]\cdot 4\text{H}_2\text{O}$ (**2**) and $(n\text{-Bu}_4\text{N})_2[\text{Pd(4-Brpma)}_2]\cdot 4\text{H}_2\text{O}$ (**3**) ($n\text{-Bu4N}^+$ = tetra-*n*-butylammonium cation), containing *N*-4-Xphenyloxamate ligands (4-Xpma with X = F, Cl and Br), where the two fragments (oxamate and Xphenyl) can be involved in hydrogen-bonding or supramolecular halogen···halogen interactions. The charge balance is ensured by bulky tetra-*n*-butylammonium cation for which it is reasonable to assume that electrostatic forces dominate conventional intermolecular interactions of the C-H···O and/or C-H···X type.[26]

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† Electronic Supplementary Information (ESI) available: Crystallographic data including Tables of H-bonds are provided (Tables S1-S6) as Supporting Information. See DOI: 10.1039/x0xx00000x

‡ Dedicated to our friend Prof. Juan Faus for his outstanding contribution to the progress of the coordination chemistry field both as teacher and researcher.

The reported results are related to our current studies on oxamato-containing metal complexes envisaging the rational design of molecule-based multifunctional materials.[27-29] Very recently, we have isolated novel palladium(II) complexes with *N*-substituted oxamate ligands and proved their activity in the sustainable palladium(II)-catalysed carbon-carbon coupling reactions, namely Suzuki and Heck reactions.[30-31] Their easy and cheap preparation, environmentally benign character and, furthermore, cytotoxic activity against leukemia cells[32] make them very appealing systems. The reaction of aqueous $[PdCl_4]^{2-}$ with *N*-4-Xphenyloxamate ligands afforded compounds **1-3**, exhibiting intriguing different three-dimensional assemblies, well driven by hydrogen bonds and/or weak C-H···O and C-H···X type interactions.[33-37] The structural study of **1** reveals that C-H···F interactions occur between the organic counterion and the fluoro substituent from the phenyl fragment, but the assembly of the complex anions is driven by C-H···$O_{oxamate}$ type interactions.[26-28] The structures of **2** and **3** shed light on the effects of the different chemical nature of Cl and Br substituents on the C-H···X interactions joined to hydrogen bonds involving oxamate oxygen atoms and crystallization water molecules. In fact, this work focus on the structural characterization of compounds **1**-**3**, special attention being paid to the supramolecular interactions that dictate and drive their crystal packing.

Experimental section

Preparation of the complexes. Compounds **1-3** were prepared as described elsewhere.[38] The recrystallization in water of powder samples of **1**-**3** afforded X-ray quality yellow prisms for all three compounds whose stoichiometry was determined by X-ray diffraction methods (see below).

X-ray data collection and structure determination. Single crystal X-ray diffraction data for **1-3** 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[39] reduction and SADABS[40] absorption software. All the structures were solved by direct methods and subsequently completed by Fourier recycling using the SHELXTL-2013[41] software packages, then refined by the full-matrix least-squares refinements based on F^2 with all observed reflections. All structures, especially in **2**, show large thermal motion on chains of *n*-tetrabutylammonium cations as often found in other complexes containing this entity. All non-hydrogen atoms were refined anisotropically, except C38 and C48 in **2**. The hydrogen atoms on the phenyl-substituted oxamate ligand and on the tetra-*n*-butylammonium cations were included at geometrically calculated positions and refined using a riding model. The hydrogen atoms on the water molecules in **2** and **3** were neither found nor calculated. Crystal data and refinements conditions for **1**-**3** are summarized in Table S1, whereas selected bond lengths and angles and hydrogen bonds are listed in Tables S2 and S3, respectively. The final graphical manipulations were carried out with the Crystal Maker programs.[42] CCDC numbers are 1408631-1408633 (**1**-**3**).

Results and discussion

Description of the structures

Compounds **1** and **3** crystallize in the monoclinic space groups *P*2$_1$/*c* and *P*2/*c*, respectively, with half a molecule in the asymmetric unit, the second half being generated by the crystallographic inversion centre. Compound **2** crystallizes in the triclinic *P*-1 space group with two half a molecule in the asymmetric unit. Each structure consists of $[Pd(4\text{-}Xpma)_2]^{2-}$ anions and *n*-Bu_4N^+ counterions (**1**-**3**) plus crystallization water molecules (**2-3**) (see Figures 1-3). The complex anions in **1** are grouped into pairs through weak C-H···O type interactions (Figure 4), these units being well separated from each other by the bulky organic cations which in turn are involved in weak C-H···F contacts (Figure 5). On the contrary, the bis(oxamate)palladate(II) species in **2** are assembled into a pretty supramolecular three-dimensional structure by means of an extended network of hydrogen bonds and C-H···Cl interactions (Figures 6-9). In the case of **3**, the complex anions are inter-connected through hydrogen bonds involving four membered rings of water molecules and leading to supramolecular anionic chains which grow along the crystallographic *a* axis (Figures 10 - 11).

The structures of **1** and **2** have in common the presence of the *trans*-$[Pd(4\text{-}Xpma)_2]^{2-}$ anions [X = F (**1**) or Cl (**2**)] where the palladium(II) ion is four-coordinate with two amidate-nitrogen [N1 and N1a] and two carboxylate-oxygen atoms [O1 and O1a] building a slightly distorted square-planar surrounding. The reduced bite angle of the chelating oxamate [81.67(6) (**1**) and 81.0(1)° (**2**)] accounts for the deviations from the ideal geometry. The Pd(II) ion and the atoms building its surrounding lie exactly on a plane for symmetry reasons. The Pd-N/Pd-O bond lengths are 2.041(2)/1.999(2) (**1**) and 2.013(3)/2.008(2) Å (**2**), values which compare well with those found in other oxamato-containing palladium(II) complexes.[30-32,38,43-45]

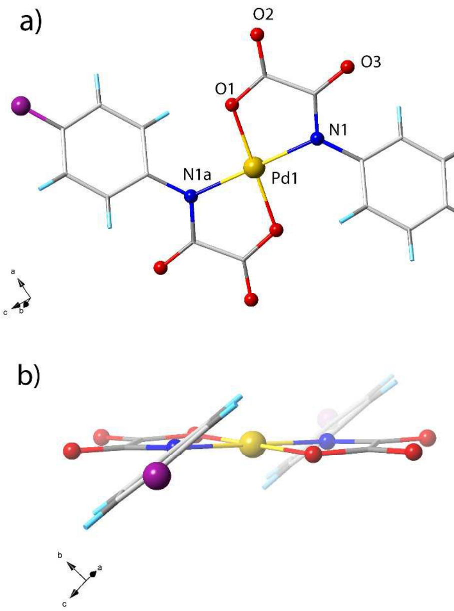

Fig. 1. Top (a) and side (b) views of *trans*-$[Pd(4\text{-}Fpma)_2]^{2-}$ complex in **1** [symmetry code: (a) = -*x*+1, -*y*+1, -*z*].

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 4.70(4) (**1**) and 4.0(2) and 0.5(2)° (**2**) for Pd1 and Pd2, respectively]. Focusing on the phenyloxamate ligand, the dihedral angle between the 4-substituted phenyl ring and the mean plane of the oxamate group are 36.71(3) (**1**) and 62.3(3) and 46.9(2)° (**2**), values which are not so close to orthogonality as those observed in $\{[Na(H_2O)]_2$*trans*-$[Pd^{II}(2,6\text{-}Me_2pma)_2]\}_n$ [ϕ = 75.79(4)] (2,6-Me_2pma = *N*-2,6-dimethylphenyloxamate),[31] but they compare well with those found in $(n\text{-}Bu_4N)_2$*trans*-$[Pd(2\text{-}Mepma)_2]\cdot 4H_2O$ and $(n\text{-}Bu_4N)_2$*trans*-$[Pd(4\text{-}Mepma)_2] \cdot 4H_2O$ [ϕ = 51.1(1) and 52.2(1)°, respectively] (2-Mepma = *N*-2-methylphenyloxamate and 4-Mepma = *N*-4-methylphenyloxamate).[30]

The $[Pd(4\text{-}Brpma)]^{2-}$ mononuclear units in the structure of **3** exhibit a *cis* conformation. However, the Pd(II) environment is practically the same of **1** and **2** being four-coordinate with two amidate nitrogen and two carboxylate-oxygen atoms from the two *cis*-oxamate ligands and building a slightly distorted square-planar [NON'O'] surrounding.

Again, the reduced bite of the chelating oxamate in **3** [81.5(1)°] accounts for the deviations from the ideal geometry. The Pd(II) ion belongs practically to its square plane. The Pd-N and Pd-O bond lengths [2.021(2)/2.008(2) Å] compare well with those found in **1** and **2** and in the already mentioned literature species.[30-32,38,43,44] The square plane at the Pd(II) and the mean plane of the chelating oxamate group in the *cis*-$[Pd^{II}(4\text{-}Brpma)_2]^{2-}$ units are very close to coplanarity as observed in **1** and **2** [the value of the dihedral angle between these two planes (*φ*) is 0.4(1)° while the dihedral angle between the 4-substituted phenyl ring and the mean plane of the oxamate group is 57.00(2)°]. Intramolecular face-to-face stacking interactions are clearly established in **3** between the phenyl rings on each chelating ligand of the *cis*-$[Pd^{II}(4\text{-}Brpma)_2]^{2-}$ unit, the two 4-substituted phenyl ring forming a dihedral angle of 14.2(1)°. This interaction together with the reduction of the polarity of C-Br bonds respect to C-X (X = F, Cl) is likely to be one of the key reasons allowing for the *cis*-arrangement of the two 4-Brpma ligands around each palladium(II) ion. Furthermore a very weak (since the two Br atoms are at a distance 0.5 Å greater than the sum of van der Walls radii) intramolecular bromo···bromo interaction [4.27 Å for Br(1)···Br(1a] would support the *cis*-conformation of the two 4-Brpma ligands observed in **3**.

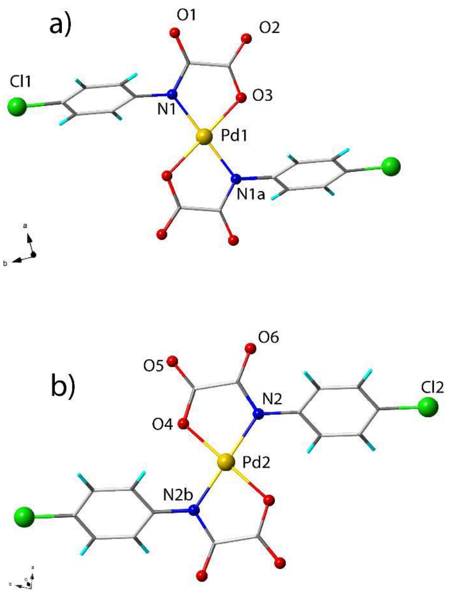

Fig. 2. Perspective view of the two crystallographically independent *trans*-$[Pd(4\text{-}Clpma)_2]^{2-}$ units in **2** [symmetry code: (a) = -*x*+2,-*y*,-*z*+1; (b) = -*x*+2,-*y*,-*z*+2].

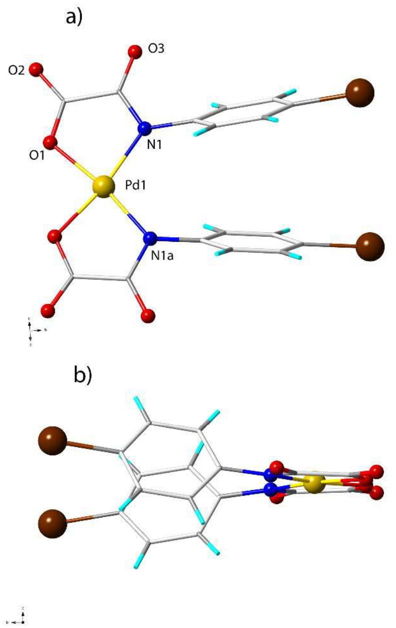

Fig. 3. Top (a) and side (b) views of the *cis*-[Pd(4-Brpma)$_2$]$^{2-}$ complex in **3** [symmetry code: (a) = -x+1 ,y, -z+1/2].

A detailed description of the different crystal packings of **1-3** is given in the following section.

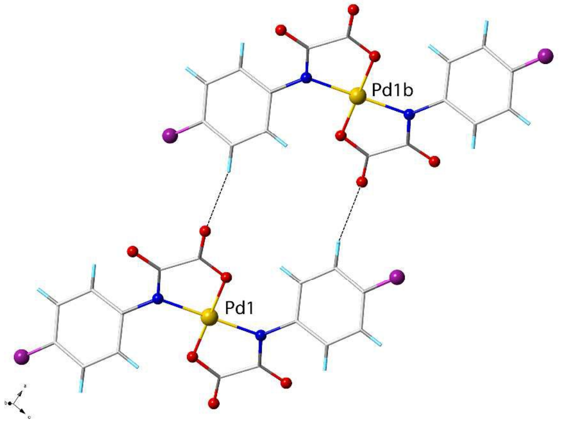

Fig. 4. Perspective view illustrating the shortest contacts between the *trans*-[Pd(4-Fpma)$_2$]$^{2-}$ anionic moieties in **1** [C-H···O = 2.722(1) Å]. Pd1···Pd1b separation of 9.645(3) Å [symmetry code: (b) = -*x*, *y*, *z*].

Crystal packing of (*n*-Bu$_4$N)$_2$*trans*-[Pd(4-F-pma)$_2$] (1)

The study of supramolecular structure of **1** shows the concomitant presence of either C-H···O or C-H···F interactions which are the driving forces towards the association of ions in the solid state.

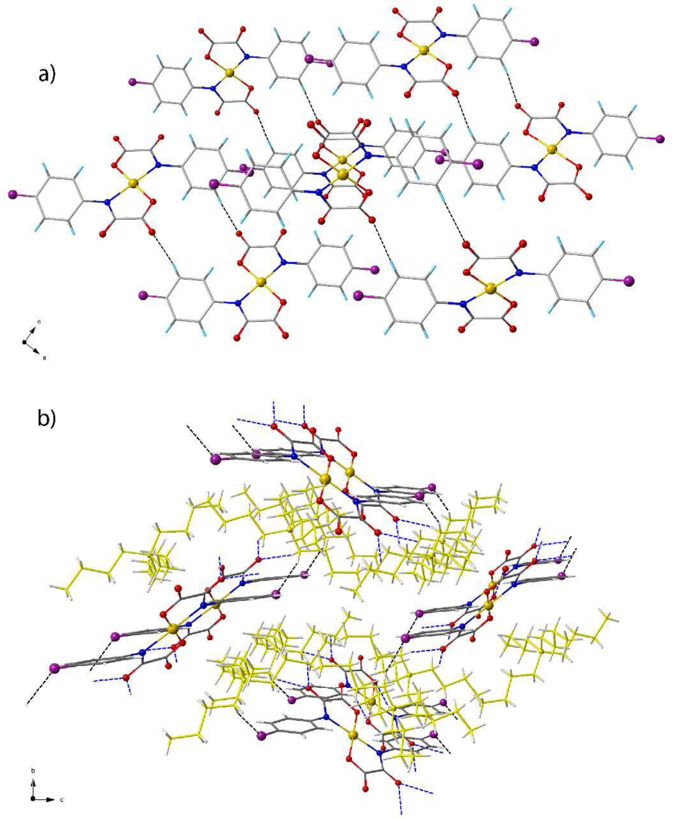

Fig. 5. A fragment of the crystal packing in **1** showing only the anionic complexes (a) and their distribution among the organic cations (b). The organic counterions have been depicted as yellow sticks and the weak CH···O and CH···F interactions as dashed blue and dark lines respectively.

In fact, the bis(oxamate)palladium(II) units are well separated from each other due to the presence of bulky (*n*-Bu$_4$N)$^+$ cations. Nevertheless, there are noticeable C$_{ph}$-H···O$_{ox}$ interactions [2.488(1) and 2.975(1) Å for H4···O1 and C4···O1 respectively, and 2.722(1) and 3.485(1) Å for H5···O2 and C5···O2] one of being related to the shortest Pd(1)···Pd(1b) separation of 9.645(3) Å [symmetry code: (b) = -*x*, *y*, *z*] (Figures 4 and 5a) and even slightly shorter C$_{cat}$-H···O$_{ox}$ interactions where the H···O distance is 2.432(1) Å [C17···H17A separation 3.338(1) Å] (Figure 5b). Furthermore, weak C-H···F interactions involving the organic *n*-Bu$_4$N$^+$ cations are present [shortest C-H···F and H···F separations of 3.381(2) and 2.468(2) Å, respectively] (Figure 5b).

Crystal packing of (*n*-Bu$_4$N)$_2$ *trans*- [Pd(4-Cl-pma)$_2$]·4H$_2$O (2)

Compound **2** shows a fascinating crystal packing due to the cooperation of different H-bonds involving also the co-crystallized water molecules and building together an elaborated supramolecular net. One of the two independent complex anions [Pd1] is engaged in such H-bond interactions between the terminal oxygen atoms of the oxamate ligand and the lattice water molecules [O$_{oxamate}$···O$_w$ distances varying in the range 2.847(3)-2.908(3) Å; see Table S5] (Figure 6)

Additional H-bonds between water molecules [O$_w$···O$_w$ distances in the range 2.664(1)-2.801(1) Å] give rise to a supramolecular 2D motif developing in the crystallographic *ab* plane, yielding a noteworthy intercalation of water chains, which are trapped in well-defined water ribbons (Figure 6).

The supramolecular three-dimensional packing is reached by means of weak C-H···Cl type interactions [C20···Cl2 and H20A···Cl2 distances of 3.502(1) and 2.955(1) Å, respectively] involving more isolated *trans*-$[Pd(4\text{-}Clpma)_2]^{2-}$moieties (Figure 7). These interactions are most likely responsible of the grasping of the two non- equivalent complex anions in **2** (Figures 7-8).

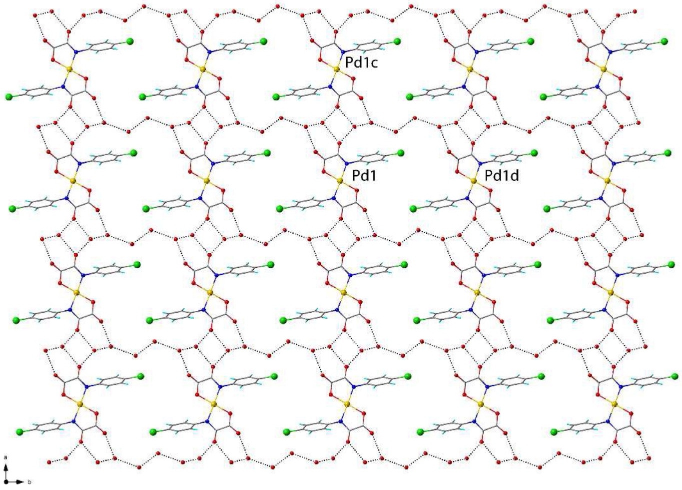

Fig. 6. View along the crystallographic *c* axis of the *trans*-$[Pd(4\text{-}Clpma)_2]^{2-}$ moieties in **2** showing intercalated water chains in a pretty sheet arrangement by mean of H-bonds and Cl···Ow type interactions. Pd(1)···Pd(1c) and Pd(1)···Pd(1d) distances equal to 12.522(1) and 15.700(1) Å, respectively [symmetry code: (c) = 2-*x*, *y*, *z*; (d) = *x*, 2-*y*, *z*].

In fact, one of the two independent complex anions [Pd2] is involved in H-bond interactions only with one of the terminal oxygen atoms of the ligand and a water lattice molecule [$O_{oxamate}$···O_w distance equal to 2.785(3) Å] (Figure 7). As shown in Figure 8, the whole packing is made up of layers with water ribbons [Pd1] staggered by other independent anions [Pd2]. The remaining voids are filled by the bulky organic countercations.

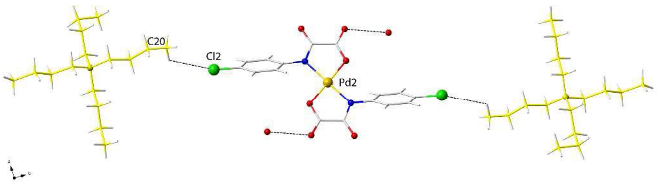

Fig. 7. Details of weak C-H···Cl type interactions [C20···Cl2 and H20A···Cl2 3.502(1) and 2.955(1) Å, respectively] in **2**.

Crystal packing of $(n\text{-}Bu_4N)_2$ *cis*-$[Pd(4\text{-}Br\text{-}pma)_2]$ · $4H_2O$ (3)

Compound **3** it is the only one containing complex anions in a *cis* conformation, namely the *cis*-$[Pd^{II}(4\text{-}Brpma)_2]^{2-}$ units. As expected for such a conformation, intramolecular face-to-face stacking interactions are clearly established between the phenyl rings on each chelating ligand of the *cis*-$[Pd^{II}(4\text{-}Br\text{-}pma)_2]^{2-}$ unit (Figure 3). The value of the centroid-centroid distance (h) between the two facing benzene rings is 3.401(1) Å, while the value of the off-set angle (φ) between the centroid-centroid vector and the normal to the plane of the benzene rings is 19.9(1)°. As mentioned above, the reduction of the polarity of C-Br bonds respect to C-X (X = F, Cl) most likely would account for the *cis*-conformation of the two 4-Brpma ligands in **3**. The steric effects produced by the adopted conformation are likely responsible for the non-zero twist angle [τ = 4.2(2)°] observed in **3** and in related compounds with *cis* stereochemistry.[31] As in **1** and **2**, C-H···X interactions involving counterions are present also in **3** [the values of C7S···Br1 and H7s1···Br1 being 3.656(1) and 2.821(1) Å, respectively] (Figure 9). These forces together with H-bonds, involving both the terminal oxygen atoms of the ligand and the lattice water molecules [$O_{oxamate}$···O_w and O_w···O_w distances of 2.817(3)-2.840(3) and 2.860(3)-2.892(3) Å, respectively; see Tables S6] give rise to a 1D supramolecular motif (Figures 10 and 11) developing along the crystallographic *a* axis. The shortest Pd···Pd separation of 8.489(1) Å corresponds to an interchain distance while the shortest intrachain separation (through the network of H-bonded water molecules) is 14.827(1) Å (Figure 11).

Adjacent supramolecular 1D motifs are disposed into a *zig-zag* arrangement leaving pseudo-hydrophobic voids to be filled by the bulky $n\text{-}Bu_4N^+$ cations (Figure 9b).

It has been found that both the *trans* and *cis* isomers of the $[Pd^{II}(4\text{-}Brpma)_2]^{2-}$ complex anion can be isolated in the solid state even if from different solvents.[38] The *trans* isomer of formula $(n\text{-}Bu_4N)_2[Pd(4\text{-}Brpma)_2]$ · H_2O crystallized as a monohydrated species[38] by slow vapor diffusion of ether into an acetonitrile solution of the complex**.** As mentioned in the experimental section suitable crystals for X-ray diffraction of **3** by recrystallization in water of the powder samples. On the contrary, we have no evidence of the formation of the *cis* isomer when $4\text{-}Fpma^{4-}$ and $4\text{-}Clpma^{4-}$ ligands were used. This result induces us to speculate on the C-X (X = F, Cl, Br) polarity as main reason. The polarity of C-Br bonds is most likely to be considerably smaller than that for C-F and C-Cl bonds. Thus, while corresponding bond dipole moments in the *trans* isomers (X = F, Cl) have opposite orientations and are likely to combine favorably in an individual mononuclear entity, leading to a low energy structure, this is much less true for the *cis* isomer (X = Br). This reduction of the bond polarity in the case of the Br derivative (**3**), may well reduce or invert the energy difference between the *cis* and *trans* isomers, and hence to be one of the key reasons, allowing the formation of the *cis* isomer with water and of the *trans* isomer in the presence of less polar solvents. In any case, being aware that different plausible reasons exist for the occurrence of the *cis* along with the *trans* isomer only in the case of the Br derivative.

Appropriate calculations which might give more insights on that matter will be further performed.

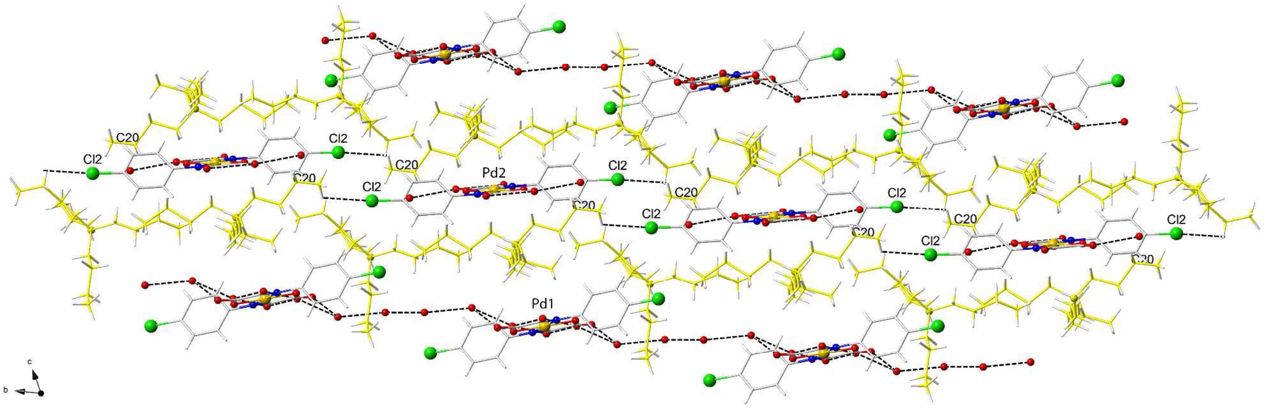

Fig. 8. View along the crystallographic *b* axis of the crystal packing of **2** showing isolated [Pd2] units interconnecting the H-bonded layers of [Pd1] units through weak C-H···Cl type interactions [the values of D···A and H···A are 3.502(1) and 2.955(1) Å, respectively]. The Pd1···Pd2 distance is 8.572(1) Å.

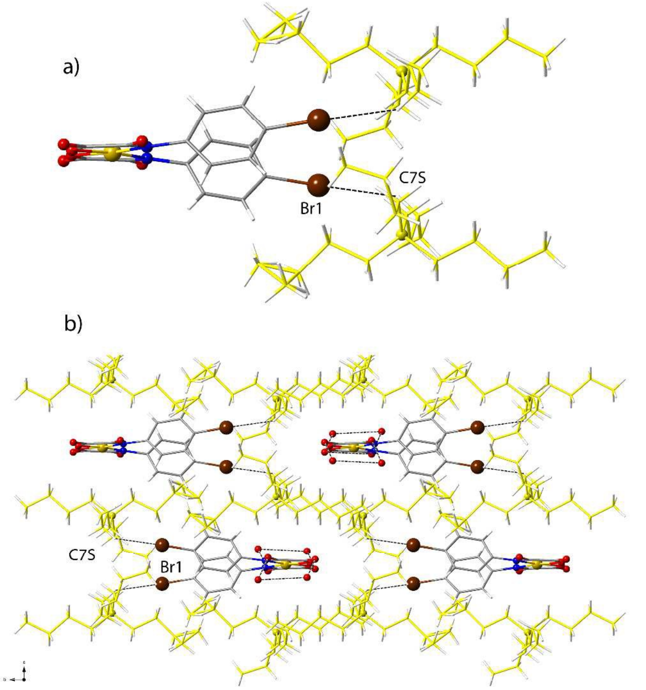

Fig. 9 View of a fragment of the structure of **3** showing the C-H···Br interactions (a) and the resulting crystal packing (b) along the crystallographic *a* axis. The whole organic counterions have been depicted in yellow [the values for C7S···Br1 and H7s1···Br1 are 3.656(1) and 2.821(1) Å, respectively].

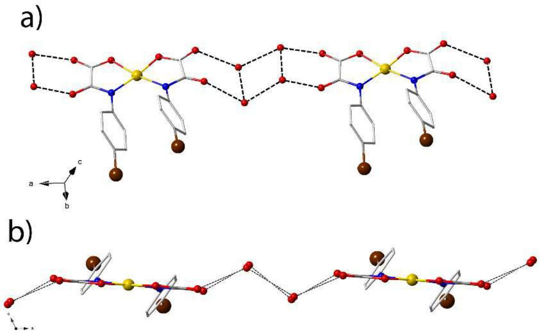

Fig. 10. Perspective (a) and side (b) views along the crystallographic *c* axis of the supramolecular chain in **3** formed through H-bonds between the *cis*-$[Pd(4\text{-}Brpma)_2]^{2-}$ unit and the crystallization water molecules.

CONCLUSIONS

In summary, concerted supramolecular motifs in fluoro-, chloro- and bromo-derivatives of the mononuclear bis-oxamatopalladate(II) complexes have been investigated. The different nature and size of the halogen atoms show a clear putative role in the supramolecular assemblies of the similar anionic complexes. These intriguing different assemblies described are undoubtedly driven by C-H···X and C-H···O type interactions together with ionic forces, (**1-3**), or combined H-bonds and C-H···X interactions (**2-3**) and/or π···π stacking and very weak interactions Br···Br (**3**) merely depending on the substitution on the ligand used. This study is a uncommon report on structural modularity of the supramolecular assemblies in *complexes as ligands* for which a modulation of supramolecular features can be achieved with a judicious choice of slightly modified ligands.

The supramolecular driving forces may be so far not all explored despite the interest in these studies, not only useful in the field of crystal engineering where insights in the prediction of the crystal structures are gained, but also in the design of new functional molecule-based materials exhibiting intriguing physical-chemical properties.

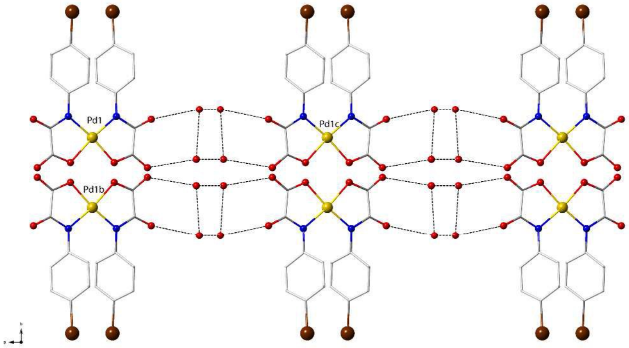

Fig. 11 View along the crystallographic *c* axis of a fragment of the supramolecular anionic chains in **3**. Pd1···Pd1b and Pd1···Pd1c distances equal to 8.489(1) and 14.827(1) Å, respectively [symmetry code: (b) = 1-*x*, *y*, 0.5-*z*; (c) = -1+*x*, *y*, *z*].

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Intermolecular interactions in dictating the self-assembly of halogen derivatives of bis-(*N*-substituted oxamato)palladate(II) complexes

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The reaction of aqueous $[PdCl_4]^{2-}$ with *N*-4-Xphenyloxamate ligands (4-Xpma with X = F, Cl and Br), afforded three non-isostructural compounds of formula $(n\text{-}Bu_4N)_2[Pd(4\text{-}Fpma)_2]$ (**1**), $(n\text{-}Bu_4N)_2[Pd(4\text{-}Clpma)_2] \cdot 4H_2O$ (**2**) and $(n\text{-}Bu_4N)_2[Pd(4\text{-}Brpma)_2] \cdot 4H_2O$ (**3**) ($n\text{-}Bu4N^+$ = tetra-*n*-butylammonium cation) exhibiting intriguing different three-dimensional assemblies, well driven by hydrogen bonds and/or supramolecular halogen···halogen interactions. Remarkable differences occur in the self-assembly of the anionic entities of **1**-**3** which are clearly dependent on the halogen substituent. In fact, the different nature and size of the halogen atoms show a clear putative role in the supramolecular assemblies of the very similar anionic complexes.