

A H-bonded Chloranilate Chain with an Unprecedented Topology

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Abstract

New $(\text{PPh}_3\text{Et})_2(\text{C}_6\text{O}_4\text{Cl}_2) \cdot 2\text{H}_2\text{O}$ (1) compound has been synthesized and structurally characterized. This compound presents layers of cations and non coordinated $[\text{C}_6\text{O}_4\text{Cl}_2]^{2-}$ anions alternating along the direction. The cationic layers contains isolated $[\text{PPh}_3\text{Et}]^+$ cations whereas in the anionic layers the chloranilate anions are connected forming chains along the a direction thanks to two H-bonds formed between the oxygen atoms of the chloranilate anions and two water molecules located between two anions. The topology of this H-bonded chain is unprecedented in any chloranilate compound. Compound 1 is the first characterized salt containing non-coordinated chloranilate anions with any phosphonium cation.

Keywords: Chloranilate dianion; Phosphonium cation; H-bond; 1D lattice; Crystal structure; Anilate; Layered structure

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Introduction

The use of the chloranilate dianion $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ (where $(\text{C}_6\text{O}_4\text{H}_2)^{2-} = 2,5$ -dihydroxy-1,4-benzoquinone derivative dianion, **(Scheme 1)** to prepare different coordination complexes and salts dates back to 1967 when E K Andersen reported the first structurally characterized chloroanilate salt: $(\text{NH}_4)_2(\text{C}_6\text{O}_4\text{Cl}_2) \cdot \text{H}_2\text{O}$ [1] and also of the chloranilic acid [2,3]. A search in the CCDC database, (updated Nov. 2014) shows a total of 328 different structures containing the chloroanilate molecule. In most of them (ca. 245 cases) chloranilate appears as the fully deprotonated $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianion, in ca. 55 cases it appears as the monoprotonated $(\text{HC}_6\text{O}_4\text{Cl}_2)^-$ anion and in ca. 30 cases it appears in the neutral $\text{H}_2\text{C}_6\text{O}_4\text{Cl}_2$ acid form. In eleven cases it is even possible to find it with two different protonation states in the same crystal. Interestingly, the three possible combinations (0/-1, -1/-2 and 0/-2) have been observed. Thus, there are four examples containing a mixture of de di-acid and the monoanion (0/-1) [4-6], two cases with a mixture of the monoanion and the dianion (-1/-2) [7,8] and five compounds combining de di-acid and the dianion (0/-2) [8-11].

If we make a survey of the coordinating ability of the chloranilate anion (either as monoanion or as dianion), we find that among the ca. 300 compounds containing any of the two anions, they appear coordinated to a metal ion in ca. 184 cases and isolated in ca. 116 compounds (half of them as the dianion and the other half

as the monoanion). In all, except two, of these ca. 184 examples where the chloranilate anions act as ligands coordinating metallic centres, the anions present the expected chelating bidentate coordination mode (1: $\kappa^2\text{O},\text{O}'$). In some cases they also coordinate an additional metal ion through only one of the oxygen atoms (1: $\kappa^2\text{O},\text{O}'$; 2: $\kappa^1\text{O}$) and in most cases they bridge two metal atoms acting as bis-chelates through both sides of the ligand (1: $\kappa^2\text{O},\text{O}'$; 2: $\kappa^2\text{O}''\text{O}'''$). The two only compounds where chloranilate is not a chelating ligand are two Mo compounds where the chloranilate bridges two Mo_2 dimers in a monodentate way (1: $\kappa^1\text{O}$; 2: $\kappa^1\text{O}'$; 3: $\kappa^1\text{O}''$; 4: $\kappa^1\text{O}'''$) [12]. Among the 182 compounds where chloranilate acts as chelate, it acts as terminal ligand (1: $\kappa^1\text{O},\text{O}'$) in only 42 cases and as bridge (1: $\kappa^2\text{O},\text{O}'$; 2: $\kappa^2\text{O}''\text{O}'''$) in 136 cases. There are four compounds where the dianion acts as terminal and as a bridge [13-15].

Among the 42 cases where chloranilate acts as terminal ligand the two most abundant metal ions are, by far, Fe [16] and Cu [17] with 13 compounds each. Other metals include Be, Cr, Co, Zr, Mo, Ru, Rh, Pd, In, Re and U. Among the 136 examples where chloranilate acts as bridging ligand there are only eight heterometallic compounds where chloranilate connects two different metals [18-21]. The remaining 128 compounds are homometallic and include all the s-block elements except Be and Mg, all the first row transition

metals except Ti, many second and third row transition metals and up to ten rare earths [15]. The most abundant metals are Cu, Mn and Co with 21, 12 and 11 examples, respectively.

Among the ca. 116 compounds where chloranilate anions are not coordinated, 109 do not contain any metal but only organic cations. Most of them (ca. 75) with N-containing heterocycles as pyridinium, pyrazinium, pyrimidinium, imidazolium, pyrazolium and ca. 30 with ammonium-type cations. Other cations include tetrathiafulvalene derivatives (4 examples) and metal complexes (7 examples). In these seven metal-containing compounds presenting isolated chloranilate anions the metals form very stable complexes with other ligands and are not available to form complexes with the chloranilate anions [10,11,22-24]. Interestingly, although there are ca. 30 examples with ammonium derivative cations, there is no example with any phosphonium derivative cation and, therefore, $(\text{PPh}_3\text{Et})_2(\text{C}_6\text{O}_4\text{Cl}_2)_2 \cdot 2\text{H}_2\text{O}$ (1) represents the first example of any chloranilate anion with a phosphonium derivative cation. Here we present the synthesis and a detailed analysis of the crystal structure of compound $(\text{PPh}_3\text{Et})_2(\text{C}_6\text{O}_4\text{Cl}_2)_2 \cdot 2\text{H}_2\text{O}$ (1), the first chloranilate salt with a phosphonium cation.

Results and Discussion

Structure of compound $(\text{PPh}_3\text{Et})_2(\text{C}_6\text{O}_4\text{Cl}_2)_2 \cdot 2\text{H}_2\text{O}$ (1)

Compound 1 crystallizes in the monoclinic P21/c space group. Its asymmetric unit contains one $[\text{PPh}_3\text{Et}]^+$ cation located on a general position, half $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ anion, located on an inversion centre, and a water molecule. **Figure 1** shows the asymmetric unit and the labelling **Scheme 1**. **Table 1** lists the crystal data and structure refinement parameters. The structure of 1 is formed by layers of $[\text{PPh}_3\text{Et}]^+$ cations parallel to the ab plane alternating along the c direction with layers containing chloranilate anions and water molecules (**Figure 2**).

The cationic layers contain ordered $[\text{PPh}_3\text{Et}]^+$ cations situated in rows along the b direction with alternating opposite orientations

in order to optimize the space filling since there is no π - π interactions between the cations (**Figure 3a**). The anionic layers contain rows parallel to the direction formed by alternating chloranilate dianions and water molecules (**Figures 3b and 4**).

The anion/water chains are held thanks to the formation of two different H-bonds. The first one is formed between the O3 atom of the chloranilate anion and the H1A of the water molecule ($\text{O3}\cdots\text{H1A} = 2.00(3) \text{ \AA}$, $\text{O1W-H1A}\cdots\text{O3} = 167.6^\circ$, $\text{O1W}\cdots\text{O3} = 2.835(2) \text{ \AA}$). The second H bond is formed between the O2 atom of the chloranilate anion and the other H atom (H1B) of the water molecule ($\text{O2}\cdots\text{H1B} = 2.09(3) \text{ \AA}$, $\text{O1W-H1B}\cdots\text{O2} = 149.8^\circ$, $\text{O1W}\cdots\text{O2} = 2.846(2) \text{ \AA}$). This second H-bond is somewhat weaker than the first one as clearly seen by the $\text{O}\cdots\text{H}$ distances and the O-H-O1W bond angles. From the $\text{O}\cdots\text{H}$ distances and the $\text{O-H}\cdots\text{O}$ angles these two H-bonds can be classified as moderate [25,26].

A careful search in the CCDC database of all the compounds where the $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianion appears non-coordinated to any metal, shows that there are only 54 of such compounds. In most cases (47) the $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianion forms H-bonds with the cations, including ten compounds where the H bonds are also formed with water molecules and two where the H-bonds are also formed with chloranilic acid molecules that also appear in the compound [8,11].

Among the only 7 compounds where the $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianion does not form any H-bond with the cations, in five cases it forms H-bond only with water molecules [10,27-30], as observed in compound 1, in one case it only forms H-bonds with chloranilic acid molecules [10] and finally, there is one compound where the $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianion appears completely isolated without forming any H-bond [22].

A close inspection at the five compounds where, as in 1, the $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianion only forms H-bonds with water molecules, shows H-bonded networks of different dimensionalities. Thus, there is one 0D case (each $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianion is connected to two water molecules which are not further H-bonded to any

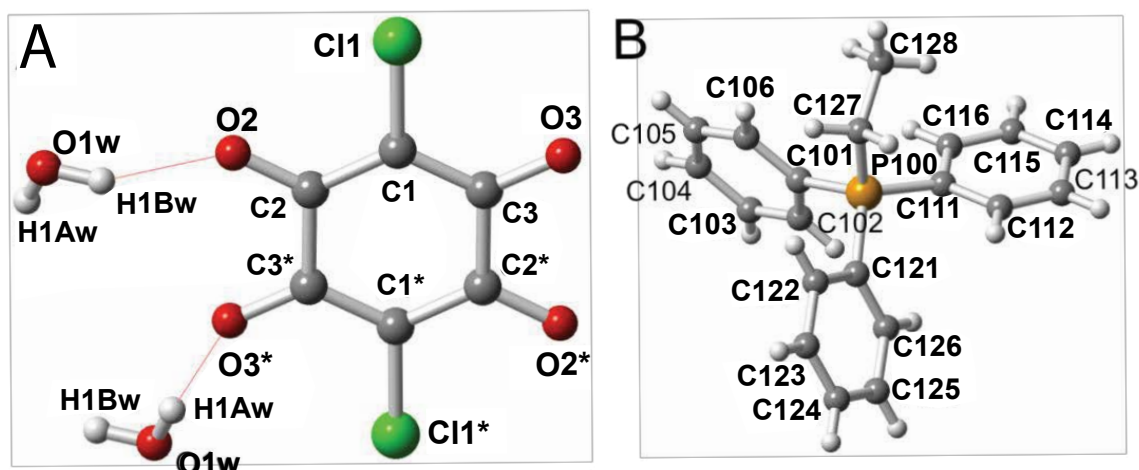


Figure 1 Labelling scheme of the anion and water molecule (A) and of the cation (B) in compound 1. The thin red lines represent the H-bonds (see text) formed between the chloranilate dianion and the water molecules.

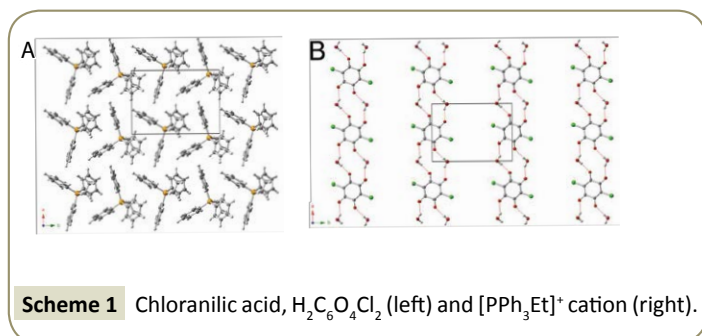
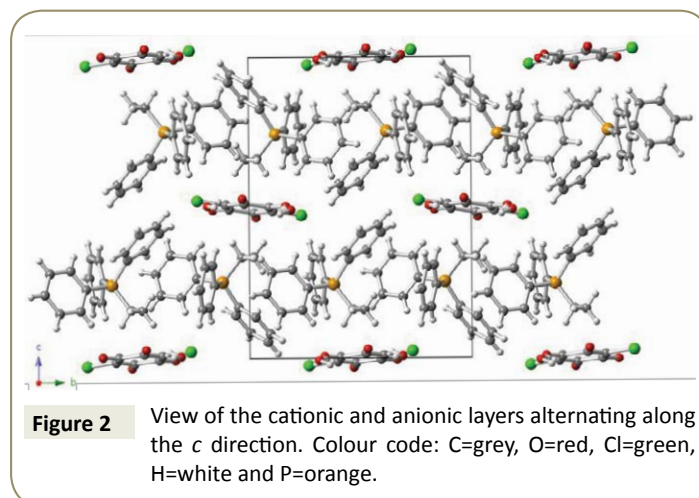


Table 1 Crystal data and structure refinement for $[\text{PPh}_3\text{Et}]_2(\text{C}_6\text{O}_4\text{Cl}_2) \cdot 2\text{H}_2\text{O}$ (1). $^{[a]}\text{R}_1(\text{F}) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$; $^{[b]}\text{wR}_2(\text{F}^2) = \frac{[\sum w(\text{F}_o^2 - \text{F}_c^2)^2 / \sum w\text{F}_o^4]^{1/2}}{\sum w\text{F}_o^2}$; $^{[c]}\text{S}(\text{F}^2) = [\sum w(\text{F}_o^2 - \text{F}_c^2)^2 / (n + r - p)]^{1/2}$

Compound	1
Empirical formula	$\text{C}_{23}\text{H}_{22}\text{ClO}_3\text{P}$
Formula weight	412.83
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
a (Å)	9.14640(10)
b (Å)	12.69380(10)
c (Å)	17.3325(2)
β (°)	94.6040(10)
Z	4
Volume	2005.85(4) Å ³
Calculated density	1.367 Mg/m ³
Absorption coefficient	0.292 mm ⁻¹
F(000)	864
Crystal size	0.18 × 0.18 × 0.10 mm
θ range for data collection	2.92–30.04°
Limiting indices	$-12 \leq h \leq 12$ $-16 \leq k \leq 17$ $-24 \leq l \leq 24$
Reflections collected / unique	65960 / 5604
R(int)	0.0534
Completeness to $\theta = 25.00^\circ$	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9714 and 0.9493
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5604 / 0 / 259
Goodness-of-fit ^[c] on F^2	0.928
Final R indices [$I > 2\sigma(I)$]	$\text{R1}^{[a]} = 0.0365$; $\text{wR2}^{[b]} = 0.0868$
R indices (all data)	$\text{R1}^{[a]} = 0.0478$; $\text{wR2}^{[b]} = 0.0965$
Largest diff. peak and hole	0.348 and -0.459 e.Å ⁻³

other molecule) [28], there are three cases where the H-bonded chloranilate dianions and the water molecules form a 2D network [10,27,30] and only one example of 1D network [29] (as observed in compound 1). The main difference between this last compound (JIXCAU) and 1 is that in 1 in each chloranilate dianion all the oxygen atoms are H-bonded to water molecules but in JIXCAU only two opposite oxygen atoms are connected and each of the oxygen atom is connected to two water molecules [29]. We can,



therefore, conclude that compound 1 has a unique H-bonded 1D topology where all the oxygen atoms of the chloranilate dianion are H-bonded to one water molecule each (Figure 5).

The bond distances and angles in the $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianion (Table 2) are similar to those found in other related compounds containing non-coordinated $(\text{C}_6\text{O}_4\text{Cl}_2)^{2-}$ dianions [10,27–30]. These bond distances and angles confirm the dianionic character of the chloranilate anion in 1.

Experimental

Synthesis of $(\text{PPh}_3\text{Et})_2(\text{C}_6\text{O}_4\text{Cl}_2) \cdot 2\text{H}_2\text{O}$ (1): A solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (213 mg, 0.8 mmol) in H_2O (5 mL) was added drop-wise to an aqueous solution (45 mL) prepared by mixing three solutions: (i) $\text{H}_2\text{C}_6\text{O}_4\text{Cl}_2$ (502 mg, 2.4 mmol) in water (25 mL) at 60°C , (ii) KOH (2 g, 35.64 mmol) in water (10 mL) and (iii) $[\text{PPh}_3\text{Et}]\text{Br}$ (891 mg, 2.4 mmol) in water (10 mL). The resulting solution was heated at 60°C for 1 h. The solution was cooled to room temperature and then extracted with three portions of CH_2Cl_2 (of 50 mL each). The resulting deep red lower CH_2Cl_2 fractions were collected and the solvent was removed by rotary evaporation. The obtained deep red lacquer solid was recrystallized with N, N-dimethylformamide (DMF) to afford 1 as red block crystals. These crystals were obtained while studying the influence of different synthetic conditions in the synthesis of tris (chloroanilate) metalate complexes of formula $[\text{M}^{\text{III}}(\text{C}_6\text{O}_4\text{Cl}_2)_3]^{3-}$ ($\text{M}^{\text{III}} = \text{Cr, Fe or Ga}$). We think that the excess of KOH in this case resulted in the formation of the hydroxido chromium (III) anionic complex $[\text{Cr}(\text{OH})_4(\text{H}_2\text{O})_2]^-$ which should not be attacked by chloranilate dianion, allowing the crystallization of this dianion with the bulky $[\text{PPh}_3\text{Et}]^+$ cation whose solubility must be lower than that of the, also known, K^+ salts of the chloranilate dianion [31].

4.2.2 X-ray structure determination of $(\text{PPh}_3\text{Et})_2(\text{C}_6\text{O}_4\text{Cl}_2) \cdot 2\text{H}_2\text{O}$ (1): A single crystal of compound 1 was covered with a layer of a viscous perfluoro-polyether (FomblinY), mounted on a cryoloop with the aid of a microscope and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 120 K on a Supernova diffractometer equipped with an Oxford Cryostream unit with mirror-monochromated and with Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved using the WINGX [32] package

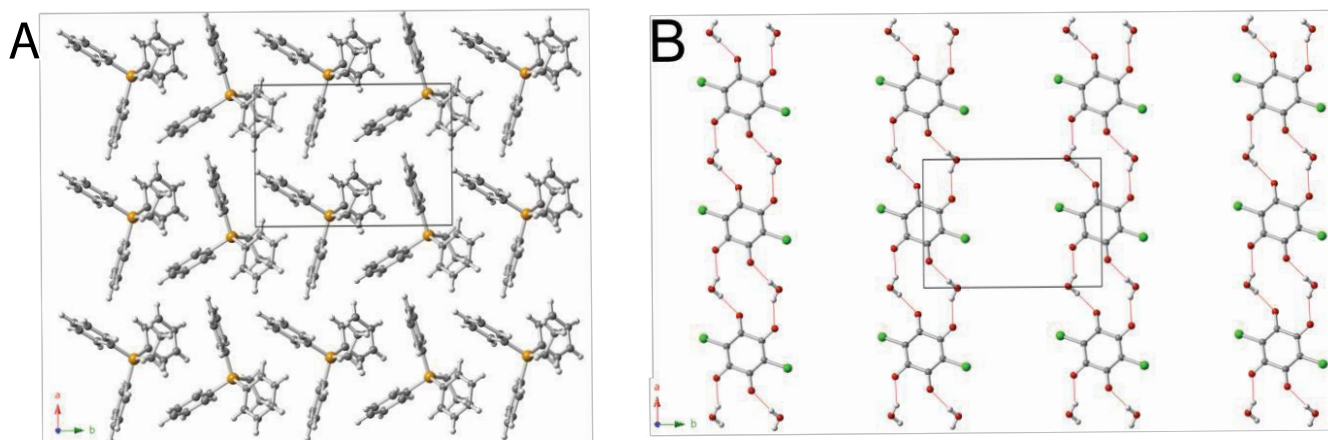


Figure 3 (A) View of the cationic layer in the *ab* plane. (B) View of the anionic layer in the same plane. Colour code: C=grey, O=red, Cl=green, H=white and P=orange.

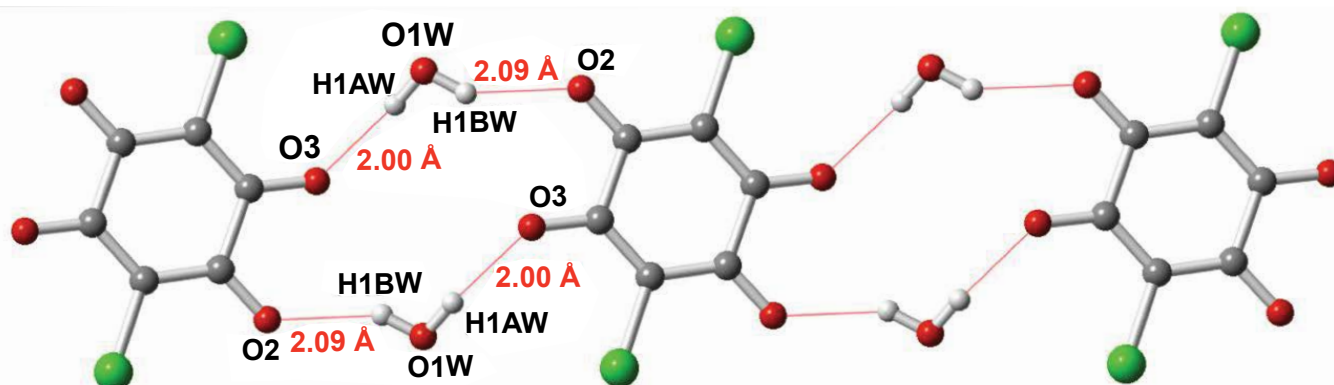


Figure 4 View of the chain formed by the chloranilate anions and the water molecules. Thin red lines are the H-bonds. The H...O bond distances are indicated in red. Colour code: C=grey, O=red, Cl=green and H=white.

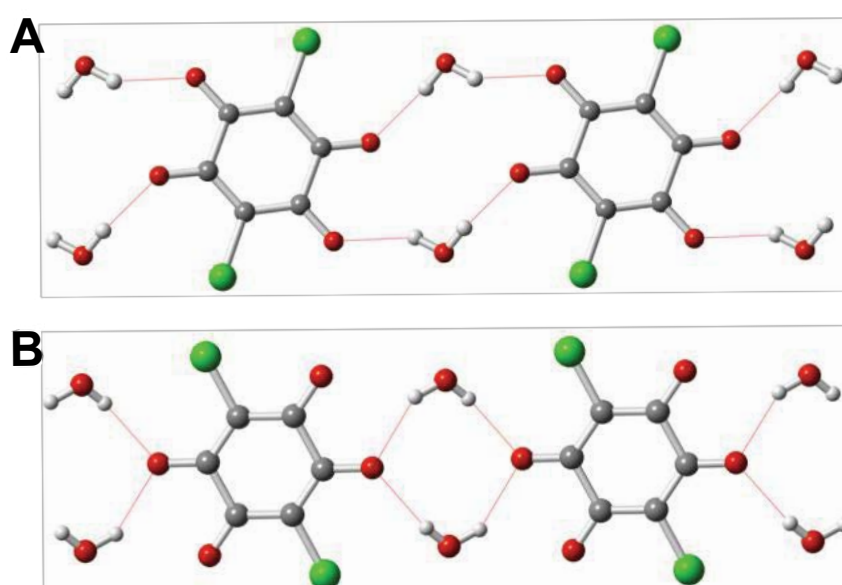


Figure 5 View of the two only known examples of 1D H-bonded lattices of chloranilate dianions and water molecules: (A) compound 1, (B) compound JIXCAU. Thin red lines represent the H-bonds. C=grey, O=red, Cl=green and H=white.

Table 2 Main bond lengths (Å) and angles (°) for $[\text{PPh}_3\text{Et}]_2(\text{C}_6\text{O}_4\text{Cl}_2) \cdot 2\text{H}_2\text{O}$ (1). Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z.

Anion			
Atoms	Distance	Atoms	Angle
C(1)-C(3) ^{#1}	1.3986(19)	C(3) ^{#1} -C(1)-C(2)	124.54(12)
C(1)-C(2)	1.4101(18)	C(3) ^{#1} -C(1)-Cl(1)	118.45(10)
C(1)-Cl(1)	1.7520(14)	C(2)-C(1)-Cl(1)	116.96(10)
C(2)-O(2)	1.2452(16)	O(2)-C(2)-C(1)	124.87(13)
C(2)-C(3)	1.5503(19)	O(2)-C(2)-C(3)	117.19(11)
C(3)-O(3)	1.2516(16)	C(1)-C(2)-C(3)	117.94(11)
C(3)-C(1) ^{#1}	1.3986(19)	O(3)-C(3)-C(1) ^{#1}	126.26(13)
		O(3)-C(3)-C(2)	116.25(12)
		C(1) ^{#1} -C(3)-C(2)	117.49(11)
Cation			
Atoms	Distance	Atoms	Distance
P(100)-C(121)	1.7912(14)	C(112)-C(113)	1.387(2)
P(100)-C(111)	1.7928(13)	C(113)-C(114)	1.391(2)
P(100)-C(101)	1.7965(14)	C(114)-C(115)	1.386(2)
P(100)-C(127)	1.8011(14)	C(115)-C(116)	1.391(2)
C(101)-C(106)	1.3989(19)	C(121)-C(122)	1.3999(18)
C(101)-C(102)	1.4010(18)	C(121)-C(126)	1.4011(19)
C(102)-C(103)	1.389(2)	C(122)-C(123)	1.3898(19)
C(103)-C(104)	1.394(2)	C(123)-C(124)	1.391(2)
C(104)-C(105)	1.388(2)	C(124)-C(125)	1.392(2)
C(105)-C(106)	1.3915(19)	C(125)-C(126)	1.3905(19)
C(111)-C(116)	1.3947(19)	C(127)-C(128)	1.531(2)
C(111)-C(112)	1.3989(19)		
Water molecule			
Atoms	Distance	Atoms	Angle
O(1W)-H(1AW)	0.86(3)	H(1AW)-O(1W)-H(1BW)	103(2)
O(1W)-H(1BW)	0.85(3)		

for CRYSLIS [33] by direct methods and refined by least squares against F^2 (SHELXL-97) [34]. Empirical absorption correction was performed using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. All non-hydrogen atoms were anisotropically refined. The hydrogen atoms were positioned geometrically and refined using a riding model, except for the H atoms of the water molecules that were located from the difference map. A summary of the data collection and structure refinement of compound 1 is provided in **Table 1**.

Conclusions

The exploration on new synthetic routes to prepare novel chloranilate-based complexes has led to the synthesis of a novel chloranilate salt containing the bulky $[\text{PPh}_3\text{Et}]^+$ cation: $(\text{PPh}_3\text{Et})_2(\text{C}_6\text{O}_4\text{Cl}_2) \cdot 2\text{H}_2\text{O}$ (1). This compound is the first chloranilate

salt with any phophonium cation and shows the formation of a 1D H-bonded network implying only the water molecules and the chloranilate dianions. Compound 1 is the second example of a 1D H-bonded network formed between chloranilate dianions and water molecules although the topology of the chain formed in 1 is unique.

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