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Crystal structure of 4-(dimethylamino)pyridin-1-ium-2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate) 4-dimethylaminopyridine (2:1) water undeca-solvate

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RESEARCH ARTICLE



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ABSTRACT

The structure of the title compound, 4-(dimethylamino)pyridin-1-ium-2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate) 4-dimethylaminopyridine water undeca-solvate, $C_{57}H_{87}Cl_5N_{12}O_{21}$, obtained from interaction between chloranilic acid (caH_2), and dimethylaminopyridine (DMAP) has been determined by single crystal X-ray diffraction. The title compound, $(DMAPH)_5(ca)_{2.5} \cdot (DMAP) \cdot 11H_2O$, crystallized in the triclinic crystal system with space group, $P\bar{1}$ (no. 2), $a = 13.3824(15)$ Å, $b = 13.4515(17)$ Å, $c = 19.048(2)$ Å, $\alpha = 86.014(4)^\circ$, $\beta = 88.821(4)^\circ$, $\gamma = 86.367(4)^\circ$, $V = 3413.3(7)$ Å³, $Z = 2$, $T = 100(2)$ K, $\mu(MoK\alpha) = 0.294$ mm⁻¹, $D_{calc} = 1.414$ g/cm³, 59413 reflections measured ($3.76^\circ \leq 2\theta \leq 56^\circ$), 16405 unique ($R_{int} = 0.0517$, $R_{\sigma} = 0.0589$) which were used in all calculations. The final R_1 was 0.0460 ($I \geq 2\sigma(I)$) and wR_2 was 0.1271 (all data). Using supramolecular chemistry principles, proton donors (chloranilic acid) and acceptor (DMAP) were combined to generate a multicomponent hydrogen-bonded system. Due to the presence of protonated bases (DMAPH⁺), the dominant interactions are the $N^+ \cdots O$ hydrogen bonds, whereas the negative charges of an acceptor from the chloranilate dianion (ca^{2-}) are delocalized. Additionally, three sets of water clusters in the title compound were identified, namely a cyclic pentamer, a linear, and an acute-shaped trimer water cluster. It was further observed that strong hydrogen bond interactions occurred between the solvated aqua molecule(s) acting as a proton donor and the neutral DMAP acting as a proton acceptor. The crystal packing is further stabilized by $O \cdots Cl$ and $C \cdots Cl$ weak halogen interactions. The lattice metric strength is further held by observed π - π stacking interactions (centroid-centroid) with inter centroid distances between sets of the DMAPH rings of 3.624(3), 3.642(4), 3.739(3), 3.863(3) and 3.898(3) Å, respectively.

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1. Introduction

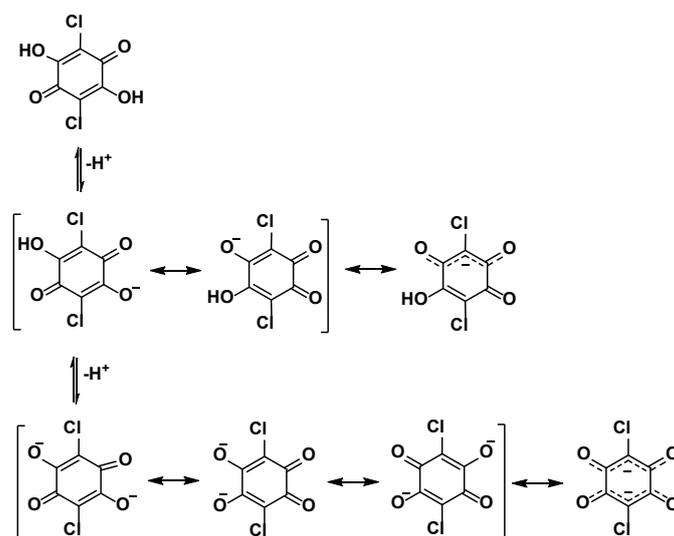
For this study, special attention was paid to choose a strong chelating ligand such as chloranilic acid (caH_2) (when deprotonated, a dianionic O, O' -bidentate ligand), which may be used to study the nature and stability of transition metal complexes, especially for hard metals i.e. Nb(V) and Ta(V) [1,2]. Crystal engineers place emphasis on the design and synthesis of preorganized ligands, which can control the structure and hence the properties of these complexes [3,4]. The scientific investigation of multicomponent crystals, involving solvates, salts, and co-crystals, provides the means to change the physicochemical properties of crystals without changing the chemical properties of the molecule of interest. Chloranilic acid and analogues (Scheme 1) represent a subclass of the quinoid compounds which are promising for the synthesis of novel functional materials. caH_2 represents a unique multifunctional ligand system because it possesses hydrogen bonding and ionic

interaction sites as well as π - π inter- and/or intra-molecular interactions, affording in principle a rich coordination chemistry. It also acts as a strong proton donor and/or acceptor [5,6]. Therefore, the investigation of the initial steps of the solvation process through the study of micro-solvated molecular systems has been an important subject for this field of chemistry [7-9].

This analysis forms part of ongoing research to investigate the mechanism of the reactions of O, O' - and N, O -bidentate ligands with transition metals used in the nuclear industry, such as Hf, Zr, Nb, Ta and some other applications [10-13]. Previously, we have reported on the novel bidentate ligand system, chloranilic acid (caH_2), a good proton donor as well as acceptor known to form complexes and co-crystals [14]. The electronic structure of chloranilic acid is susceptible to different degrees of deprotonation and various modes of proton transfer under applied experimental conditions, see Scheme 1.

Table 1. Crystal data and details of the structure refinement for the title compound, (DMAPH)₅(ca)_{2.5}·11H₂O.

Parameters	Compound
Empirical formula	C ₅₇ H ₆₇ Cl ₅ N ₁₂ O ₂₁
Formula weight	1453.64
Temperature (K)	100(2)
Crystal system	Triclinic
Space group	<i>P</i> 1
<i>a</i> (Å)	13.3824(15)
<i>b</i> (Å)	13.4515(17)
<i>c</i> (Å)	19.048(2)
α (°)	86.014(4)
β (°)	88.821(4)
γ (°)	86.367(4)
Volume (Å ³)	3413.3(7)
<i>Z</i>	2
ρ_{calc} (g/cm ³)	1.414
μ (mm ⁻¹)	0.294
<i>F</i> (000)	1532.0
Crystal size (mm ³)	0.252 × 0.173 × 0.130
Radiation	MoK α (λ = 0.71073 Å)
2 θ range for data collection (°)	3.76 to 56.00
Index ranges	-12 ≤ <i>h</i> ≤ 17, -17 ≤ <i>k</i> ≤ 17, -24 ≤ <i>l</i> ≤ 25
Reflections collected	59413
Independent reflections	16405 [<i>R</i> _{int} = 0.0517, <i>R</i> _{sigma} = 0.0589]
Data/restraints/parameters	16405/0/852
Goodness-of-fit on <i>F</i> ²	1.003
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0460, <i>wR</i> ₂ = 0.1052
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0847, <i>wR</i> ₂ = 0.1271
Largest diff. peak/hole (e Å ⁻³)	0.38/-0.34

**Scheme 1.** Dissociation of chloranilic acid (caH₂) to the monoanion (caH⁻) and dianions (ca²⁻), with resonance structures shown in brackets (*pK*_{a1} = 0.76 and *pK*_{a2} = 2.58) [15]. Intramolecular electron delocalizations in the mono- and di-anions are also shown.

Herein, we report the synthesis and characterization of a new co-crystal structure of the hydrous 1:2 multi-hydrate compound of chloranilic acid with 4-*N,N*-dimethyl aminopyridine (DMAP), which was investigated by single-crystal X-ray diffraction at 100(2) K (Table 1).

During crystallization, there were four components involved: the 4-(dimethylamino)pyridin-1-ium cations (DMAPH⁺) which combine in a 2:1 ratio with the 2, 5-dichloro-3, 6-dioxo cyclohexa-1,4-diene-1,4-bis(olate)dianion (trivial name chloranilate dianion) (ca²⁻), one DMAP, and 11 water molecules. Herein, the determination of the structure of the title compound forms part of our systematic investigation concerning π - π stacking interactions, infinite hydrogen bond networks, and halogen bond networks within this interesting bidentate ligand system.

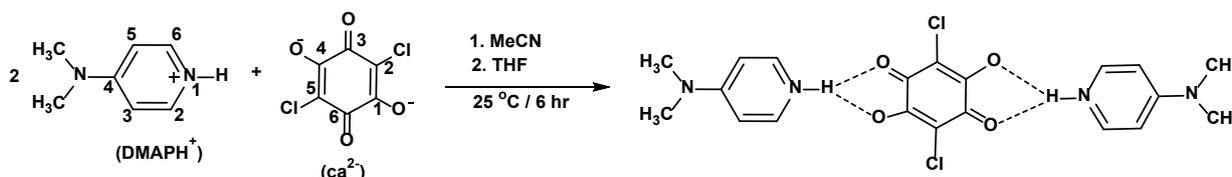
2. Experimental

All the chemicals and solvents used were of analytical grade purchased from Sigma-Aldrich, South Africa. Reagents were

used as received without further purification. The infrared spectra of the complexes were recorded on a Bruker Tensor 27 Standard System spectrophotometer utilizing a He-Ne laser at 632.6 nm in a range of 4000-600 cm⁻¹. The sample was analysed as solid-state species via Attenuated Total Reflection (ATR) mode infrared spectrophotometry and the data was recorded at room temperature. No solution or KX (where X = I, Cl, Br) solid salt pellets were utilized because halogen interaction was expected from the solution cell and the KX pellet preparation technique. The ¹H and ¹³C NMR spectra were recorded on a Bruker Fourier 300 MHz (¹H: 300.18 MHz; ¹³C: 75.48 MHz) (5 mm, ¹³C/¹H high-resolution NMR probe equipped with Z-gradient coil) nuclear magnetic resonance spectrometer operating at 25 °C. Chemical shifts are reported relative to tetramethylsilane (TMS) as an internal standard using the CD₃OD or the solvent peaks, (¹H NMR: 3.31 ppm; ¹³C NMR: 49.1 ppm) peaks. The abbreviations s = singlet and d = doublet are used throughout.

Table 2. Selected bond lengths and angles of (DMAPH)₅(ca)_{2.5}(DMAP)·11H₂O.

Bond lengths (Å)			
C2A-O1A	1.265(1)	C4A-Cl2A	1.732(1)
C3A-O2A	1.246(1)	C7A-Cl3A	1.742(1)
C5A-O3A	1.254(1)	C10A-Cl4A	1.735(2)
C6A-O4A	1.242(1)	C14A-Cl5A	1.736(1)
C8A-O5A	1.252(1)	C5B-N1B	1.341(1)
C9A-O6A	1.255(1)	C10B-N4B	1.344(1)
C11A-O7A	1.253(1)	C19B-N5B	1.338(1)
C12A-O8A	1.241(1)	C26B-N8B	1.342(1)
C13A-O9A	1.251(1)	C33B-N10B	1.363(1)
C15A-O10A	1.249(1)	C40B-N12B	1.341(1)
C1A-C11A	1.738(1)		
Bond angles (°)			
C3B-N2B-C7B	119.83(2)	C28B-N7B-C24B	120.09(2)
C12B-N3B-C13B	120.17(2)	C35B-N9B-C31B	114.85(2)
C17B-N6B-C21B	120.25(2)	C42B-N11B-C38B	120.52(2)

**Scheme 2.** Representation of ligands (DMAPH⁺ and ca²⁻, (2:1)) and the reaction for the formation of [(DMAPH)₂(ca)].

2.1. Synthesis of 4-(dimethylamino)pyridin-1-ium-2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate) 4-dimethylaminopyridine (2:1) water undeca-solvate (DMAPH)₅(ca)_{2.5}(DMAP)·11H₂O

2, 5-Dichloro-3, 6-dihydroxy-2, 5-cyclohexadiene-1,4-dione (caH₂) (0.0750 g, 0.3591 mmol) was dissolved in tetrahydrofuran (5 mL), and treated with 4-*N,N*-dimethylaminopyridine, DMAP (0.0876 g, 0.7172 mmol) in acetonitrile (5 mL) at room temperature. The resulting mixture was stirred for 6 h, and the volatile material was removed in vacuo (Scheme 2). Color: Deep purple powder. Yield: 0.13 g, 78.5%. FT-IR (ATR, ν, cm⁻¹): 1750-3089 (N-H...O). UV/Vis (CH₃OH, λ_{max}, nm, ε): 524 (1.755×10³ M⁻¹cm⁻¹). ¹H NMR (300 MHz, CD₃OD, δ, ppm): 8.11 (d, 4H, py), 6.98 (d, 4H, py), 3.26 (s, 12H, CH₃). ¹³C NMR (75 MHz, CD₃OD, δ, ppm): 166.47 (C=O; C-OH, caH₂), 158.35, 138.58, 107.57 (py) 106.79 (C-Cl, caH₂).

2.2. Crystal growth

Cuboid crystals of the title compound, 4-(dimethylamino)pyridin-1-ium-2, 5-dichloro-3, 6-dioxocyclohexa-1,4-diene-1,4-bis(olate) 4-dimethylaminopyridine (2:1) water undeca-solvate were grown from a solution of the product in a mixture of acetonitrile and methanol (3:2, v:v) using a slow evaporation technique; the solution was left to stand at 255 K for a few days and crystals suitable for X-ray diffraction were obtained.

2.3. Single-crystal X-ray data collection, reduction, and refinement

X-ray intensity data was collected on a Bruker X8 Apex II 4K Kappa CCD area detector diffractometer, equipped with a graphite monochromator and MoKα fine focus sealed tube (λ = 0.71073 Å, T = 100(2) K and 298(2) K) operated at 2.0 kW (50 kV, 40 mA). The initial unit cell determinations and data collection were done using the APEX2 [16] software package. The collected frames were integrated using a narrow-frame integration algorithm and reduced with the Bruker SAINT Plus and XPREP software packages [17], respectively. Analysis of the data showed no significant decay during the data collection. The data was corrected for absorption effects using the multi-scan technique SADABS [18] and the structure was solved by the

direct methods package SIR-97 [19] and refined using the WinGX [20] software incorporating SHELXL [21]. The aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C-H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C), for methyl C-H of 0.96 Å (C-H) [*U*_{iso}(H) = 1.5 *U*_{eq}]. The highest peak (0.38 e.Å⁻³) is located 0.63 Å from C4B and the deepest hole (-0.33 e.Å⁻³) is situated 0.26 Å from H11D. All non-hydrogens were refined anisotropically. Hydrogens were placed geometrically at calculated positions on their carrier atoms and refined with a riding model. That is, the hydrogen atoms of 11 solvated water molecules found in the compound were nicely refined and all atoms are best fit the electron density from the Fourier map. Refinement of *F*² against all reflections. The weighted *R*-factor *wR*₂ and goodness-of-fit *S* are based on *F*², the conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative *F*². The threshold expression of *F*² > 2σ (*F*²) is used only for calculating *R* factors (gt) and is not relevant to the choice of reflections for refinement. *R*-factors based on *F*² are statistically about twice as large as those based on *F*, and *R*-factors based on all data will be even larger. Non-hydrogen atoms were refined with anisotropic displacement parameters. The graphics were done using the DIAMOND and OLEX2 [22,23] program with 50% probability displacement ellipsoids for all non-hydrogen atoms.

3. Results and discussion

3.1. Molecular structure

To complete the structural characterization, the exact molecular structure of the title compound was obtained by X-ray diffraction analysis. The structure of 4-(dimethylamino)pyridin-1-ium-2, 5-dichloro-3, 6-dioxocyclohexa-1,4-diene-1,4-bis(olate) 4-dimethylaminopyridine (2:1) water undeca-solvate is shown in Figure 1. The selected bond lengths and angles of (DMAPH)₅(ca)_{2.5}(DMAP)·11H₂O are given in Table 2. The title compound, (DMAPH)₅(ca)_{2.5}(DMAP)·11H₂O crystallizes in the triclinic space group, *P* $\bar{1}$, with *Z* = 2. The asymmetric unit of this compound contains five 4-(dimethylamino)pyridin-1-ium cations (DMAPH⁺) and one 4-*N,N*-dimethylaminopyridine (DMAP); two and a half 2,5-dichloro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate) dianion (trivial name chloranilate dianion) entities; as well as one half of a chloranilate dianion (ca²⁻), sitting on an

Table 3. The selected hydrogen bond distances and angles of (DMAPH)₅(ca)_{2.5}·(DMAP)·11H₂O.

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	D-H...A (°)
O7W-H7WA...O8W	0.85	1.90	2.753	176(3)
O1-H1A...O10W	0.85	1.86	2.695	170
O1-H1B...O7A	0.85	1.97	2.822	175
O7W-H7WB...O5A	0.85	1.92	2.767	176(2)
N2B-H2B...O1A	0.94	2.04	2.793	135
N2B-H2B...O2A	0.94	2.01	2.821	143
O5W-H5WA...O1A	0.85	1.99	2.842	171
O5W-H5WB...O6W	0.85	1.86	2.707	173(2)
O4W-H4WA...O3W	0.85	1.91	2.755	172(3)
O4W-H4WB...O5W	0.85	1.95	2.783	168
N6B-H6B...O5A	0.85	2.32	2.964	133
N6B-H6B...O6A	0.85	1.96	2.734	151
O6W-H6WA...C15A ⁱ	0.85	2.81	3.463	136
O6W-H6WA...O10A ⁱ	0.85	2.13	2.905	152
O6W-H6WB...O7W	0.85	1.89	2.730	1.73
O1W-H1WA...N9B	0.85	2.06	2.898	167
O1W-H1WB...C12A ⁱⁱ	0.85	2.76	3.263	119
O1W-H1WB...O2A ⁱⁱ	0.85	2.23	3.044	161
O10W-H10A...O4A ⁱⁱⁱ	0.85	2.08	2.877	157
O10W-H10B...O11W ^{iv}	0.85	1.87	2.710	168
O8W-H8WA...O4W	0.85	1.93	2.774	172
N11B-H11B...O9A ^v	0.89	2.20	2.913	137
N11B-H11B...O10A	0.89	1.99	2.758	144
O11W-H11C...O9A	0.85	1.97	2.812	172(3)
O11W-H11D...O1	0.85	1.88	2.715	167
O8W-H8WB...O3A ⁱⁱ	0.85	2.02	2.859	169
O2W-H2WA...C14A ^{vi}	0.85	2.82	2.821	121
O2W-H2WA...O6A ^{vi}	0.85	2.01	2.013	164
O2W-H2WB...O1W	0.85	2.03	2.029	172
O3W-H3WA...O1A ^{vii}	0.85	2.18	2.964	154
O3W-H3WB...O2W	0.85	1.89	2.729	170
N7B-H7BA...O7A	0.94	2.03	2.821	141
N7B-H7BA...O8A	0.94	2.05	2.815	138
N3B-H3BA...O3A	0.92	2.18	2.902	135(2)
N3B-H3BA...O4A	0.92	1.99	2.789	145
C12B-H12B...O7W ^{viii}	0.93	2.57	3.188	124
C21B-H21B...O8W	0.93	2.61	3.257	128
C29B-H29B...C13A ^{ix}	0.96	2.98	3.929	170
C37B-H37A...C11A ^x	0.96	2.92	3.718	141(2)

Symmetry code: (i) $-x+1, -y+1, -z$, (ii) $x+1, y, z$, (iii) $x, y+1, z$, (iv) $-x+1, -y+1, -z$, (v) $-x, -y+2, -z$, (vi) $-x+2, -y+1, -z+1$, (vii) $-x+2, -y, -z+1$, (viii) $x-1, y, z$, (ix) $x+1, y, z+1$, (x) $-x, -y+1, z-1$.

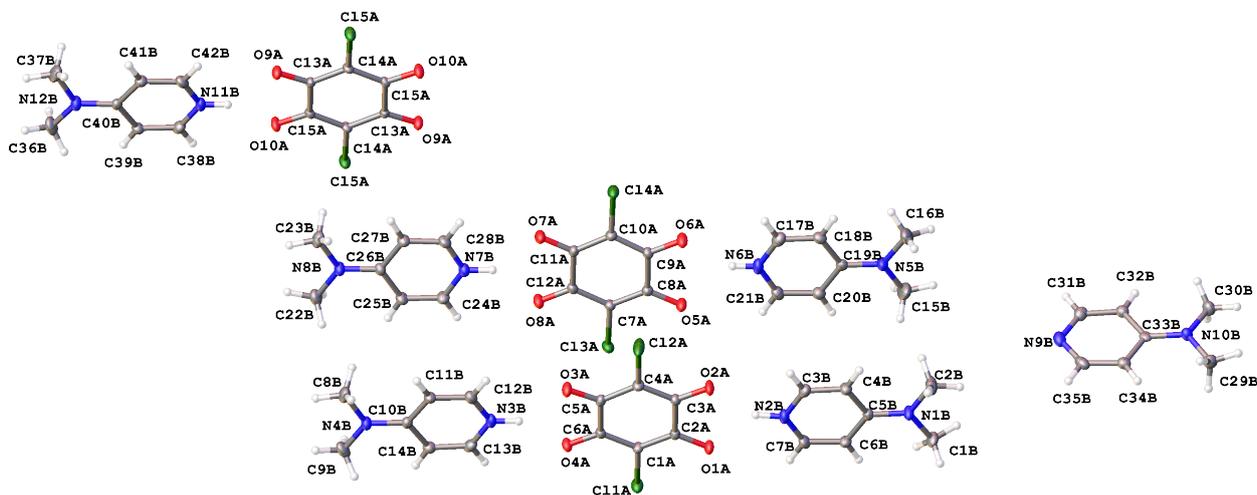


Figure 1. The molecular structure of (DMAPH)₅(ca)_{2.5}·(DMAP)·11H₂O. Thermal ellipsoids are drawn at 50% probability displacements. The atom numbering is shown and water molecules have been omitted for clarity.

inversion center and its symmetry generated counterparts are linked by the network of extended hydrogen bonds to the 4-(dimethylamino)pyridin-1-ium cations (DMAPH) and solvated aqua cluster molecules. There are five protonated DMAPH⁺ moieties (out of six) inducing a positive charge population in the unit cell which effectively balances with the ligand co-crystal (*cf.* Figures 1-3). Therefore, due to the presence of protonated bases (DMAPH⁺), the dominant interactions are the N⁺-H...O hydrogen bonds, whereas the negative charges of an

acceptor from the chloranilate dianion (ca²⁻) are delocalized. It was found that the guest donor, DMAP, co-crystallizes with chloranilic acid (caH₂) through hydrogen bonding between protonated DMAPH⁺ and the dianion of chloranilic acid acting as an acceptor to the nitrogen donor group of the DMAP, via an infinite network of N-H...O hydrogen-bonds (*cf.* Figure 2A). Additionally, we found a strong hydrogen bond interaction between the solvated aqua molecules acting as a proton donor and the neutral DMAP (unprotonated DMAP) acting as a proton

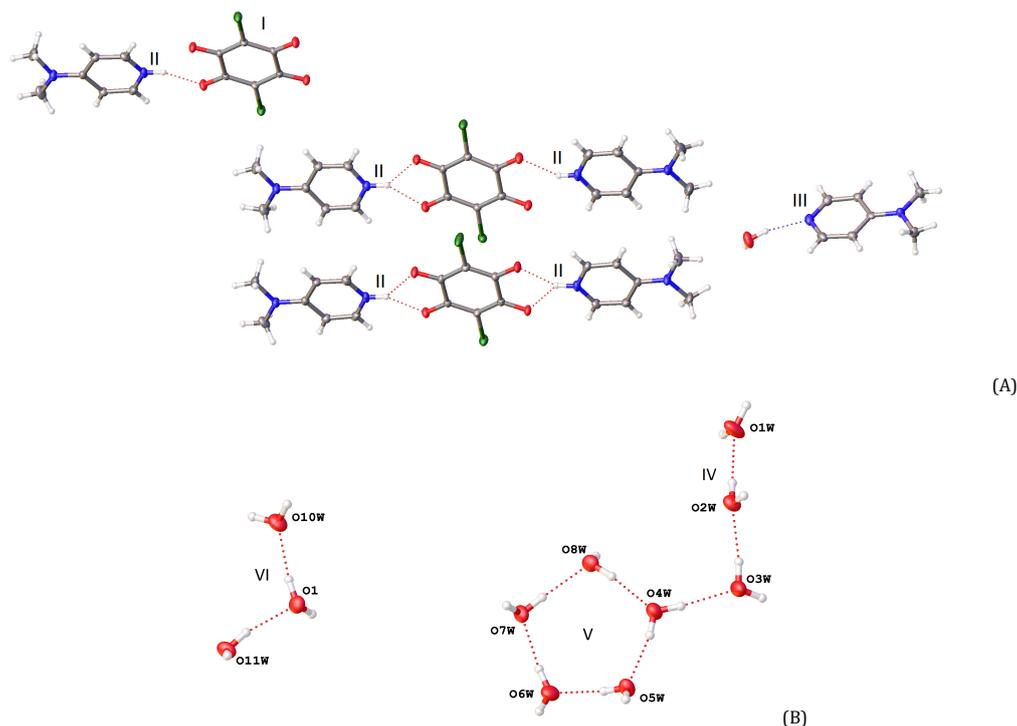


Figure 2. (A) Molecular structure of $(\text{DMAPH})_5(\text{ca})_{2.5}(\text{DMAP}) \cdot 11\text{H}_2\text{O}$ showing the head-to-tail network of infinite intermolecular interactions, with water molecules omitted. (B) Water clusters shown with respective hydrogen interactions with other atoms omitted for clarity. Non-hydrogen atoms are drawn at 50% probability displacement ellipsoids are used. The red dashed lines indicate $\text{O-H}\cdots\text{O}$, $\text{O-H}\cdots\text{N}$, $\text{N-H}\cdots\text{O}$, $\text{C-H}\cdots\text{O}$, and $\text{O-H}\cdots\text{Cl}$, $\text{C-H}\cdots\text{Cl}$, hydrogen and halogen interactions, respectively, as well as cyclic pentamer (V) and linear (IV) and acute shaped (VI) trimer water clusters. The roman numerical of I, II, and III indicates half a ligand with only one charge, protonated DMAPH and neutral DMAP, respectively.

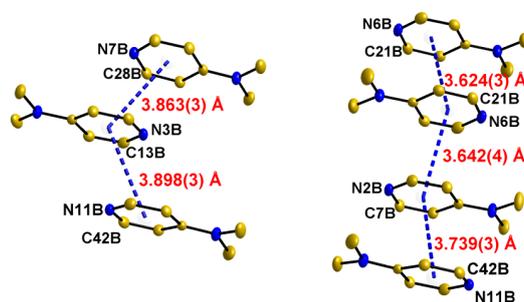


Figure 3. Molecular structure of $(\text{DMAPH})_5(\text{ca})_{2.5}(\text{DMAP}) \cdot 11\text{H}_2\text{O}$ showing the head to tail network of infinite intermolecular interactions. The blue dashed lines indicate the π - π stacking interaction [centroid-centroid = 3.624(3) Å (i), 3.642(4), 3.739(3) Å (ii), 3.863(3) and 3.898(3) Å] distance between two DMAPH⁺ rings on N6B-C21B and symmetrically generated N6B-C21B, N2B-C7B and N6B-C21B, N2B-C7B and N11B-C42B as well as N3B-C13B and symmetrically generated N3B-C13B, N7B-C28B and N3B-C13B, N11B-C42B [Symmetry codes: (i) -x, -y, 1-z, (ii) 1-x, 1-y, 1-z]. H atoms are omitted for clarity.

acceptor; $\text{O-H}\cdots\text{O}$, $\text{O-H}\cdots\text{N}$, $\text{N-H}\cdots\text{O}$, and $\text{C-H}\cdots\text{O}$ hydrogen bonds and $\text{O-H}\cdots\text{Cl}$ and $\text{C-H}\cdots\text{Cl}$ halogen bonds (cf. the Figure 2A, and 2B and Table 3). This generates infinite hydrogen- and halogen bonding networks. Hydrogen and halogen bonds are used as “supramolecular glue” in the construction of these molecular architectures and water solvent molecules as connectors and/or stabilizers. The crystal packing is reinforced by the formation of an extensive network of halogen and hydrogen bonds as with similar work reported earlier.

3.2. Supramolecular features

The title compound is stabilized further by a cluster of eleven aqua units. This generates an infinite network of hydrogen bonds which can be characterized as strong and weak hydrogen bond interactions. Different v-shaped bifurcated strong hydrogen bonds are present, which show H3Ba bonded to O3A and O4A, H7Ba bonded to O7A and O8A, H2B bonded to

O1A and O2A between protonated DMAPH⁺ cations and the chloranilate dianion (ca^{2-}) molecules. We identified three sets of water clusters in the title compound, namely a cyclic pentamer (O4W-O5W-O6W-O7W-O8W), a linear trimer (O1W-O2W-O3W) and an acute-shaped trimer (O10W-O1-O11W) water cluster interactions (cf. Figure 2B; V, IV and VI, respectively). The measured angles of the linear trimer and the acute-shaped trimer water clusters are 141.38(1) and 110.99(1)°, respectively. Resulting from the cyclic pentamer water cluster interactions, five different angles between O4W-O5W-O6W, O5W-O6W-O7W, O6W-O7W-O8W, and O7W-O8W-O4W can be observed and are 99.64(9), 108.95(9), 107.92(1), 100.53(9) and 114.26(9)°, respectively. These molecules of water are positioned midway between the protonated DMAPH⁺ entities and the chloranilate dianions (ca^{2-}), which are each involved in the cyclic pentamer, linear trimer, and acute-shaped trimer, respectively. Such network structures stabilize the crystal lattice. It is especially interesting to note that the water

cluster units are strongly held together by O-H...O and O-H...N interactions with the O...O distance ranging from 2.695(3) to 5.287(5) Å and the O...O angle ranging from 99.64(9) to 141.38(1)°. The infinite water clusters are linked by a strong O-H...Cl hydrogen bond. Inter- and intramolecular hydrogen-bonds and halogen-bonds were observed in the range of (i) O-H...O (1.85(2)-1.97(2) Å, (ii) O-H...N (2.06 Å), (iii) N-H...O (1.96(2)-2.32(2) Å, (iv) C-H...O (2.57(3)-2.60(3) Å, and (v) O-H...Cl (2.76(2)-2.81(2) Å, as well as (vi) C-H...Cl (2.92(3)-2.98(3) Å, respectively (cf. Figure 2). Therefore, the hydrogen bond N⁺-H...O with a delocalized negative charge of an acceptor from the chloranilate dianion characterizes these systems. However, C-H...Cl interactions involving the chloranilic anion skeleton are very rare (Table 3).

In addition to the intermolecular interactions described, the molecules are linked together by symmetry-related π - π stacking interactions (centroid-centroid), with distances between respective sets of DMAPH⁺ rings 3.624(3), 3.642(4), 3.739(3), 3.863(3) Å and 3.898(3) Å (cf. Figure 3), formed by the DMAPH⁺ rings labeled as Cg3-Cg3, Cg1-Cg3, Cg1-Cg5, Cg4-Cg2 and Cg2-Cg5, respectively; where Cg1 (N2B-C7B), Cg2 (N3B-C13B), Cg3 (N6B-C21B), Cg4 (N7B-C28B) and Cg5 (N11B-C42B).

4. Conclusions

The co-crystalline compound, 4-(dimethylamino)pyridin-1-ium-2, 5-dichloro-3, 6-dioxocyclohexa-1, 4-diene-1, 4-bis(olate) 4-dimethylaminopyridine water undeca-solvate was successfully synthesized and its structure confirmed by single crystal X-ray diffraction and spectroscopic techniques (FT-IR, ¹H and ¹³C NMR). The molecular structure of this new compound, as determined by single-crystal X-ray diffraction, is stabilized by a cluster of eleven aqua units. This generates an infinite network of hydrogen and halogen bonds which can be characterized as strong and weak interactions.

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Supporting information

CCDC-2021605 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.



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References

- [1]. Kawaguchi, H.; Matsuo, T. *J. Organomet. Chem.* **2004**, *689*, 4228-4243.
- [2]. Bruijninx, P.; Viciano-Chumillas, M.; Lutz, M.; Spek, A.; Reedik, J.; van Koten, G.; Klein Gebbink, R. *Chem. Eur. J.* **2008**, *14*(18), 5567-5576.
- [3]. Elhabiri, M.; Haracek, J.; Bünzli, J.; Gary, A. *Eur. J. Inorg. Chem.* **2004**, 51-62.
- [4]. Kim, J.; Hong, M.; Ahn J.; Lee, M. *Angew. Chem. Int. Edn.* **2005**, *44*, 328-332.
- [5]. Molcanov, K.; Kojic-Prodicand, B.; Meden, A. *Croat. Chem. Acta.* **2009**, *82*(2), 387-396.
- [6]. Sandeep, G.; Biprajit, S.; Somnath, M.; Vedavati, G. P.; Jan, F.; Francisco, A. U.; Reyes, J. A.; Wolfgang, K.; Goutam, K. L. *Chem. Eur. J.* **2008**, *14*(34), 10816-10828.
- [7]. Desfrancois, C.; Carles, S.; Schermann, J. P. *Chem. Rev.* **2000**, *100*, 3943-3962.
- [8]. Dopfer, O.; Fujii, M. *Chem. Rev.* **2016**, *116*, 5432-5463.
- [9]. Becucci, M.; Melandri, S. *Chem. Rev.* **2016**, *116*, 5014-5037.
- [10]. Belay, A. N.; Koen, R.; Drost, R. M.; Venter, J. A. *Z. Kristallogr. NCS.* **2016**, *231*(2), 513-515.
- [11]. Herbst, L.; Visser, H. G.; Roodt, A. *Adv. Mat. Res.* **2014**, *1019*, 412-418.
- [12]. Koen, R.; Roodt, A.; Visser, H. G. *Adv. Mat. Res.* **2014**, *1019*, 426-432.
- [13]. Schutte, M.; Kemp, G.; Visser, H. G.; Roodt, A. *Inorg. Chem.* **2011**, *50*, 12486-12498.
- [14]. Belay, A. N.; Venter, J. A.; Roodt, A. *Z. Kristallogr. NCS* **2017**, *232*(2), 163-164.
- [15]. Sahar, I. M. *Transition Met. Chem.* **1999**, *24*, 306-310.
- [16]. Bruker Apex2 (Version 2011. 4-1), Bruker AXS Inc., Madison, Wisconsin, USA, 2011.
- [17]. Bruker SAINT-Plus (Version 6. 02 including XPREP), Bruker AXS Inc., Area-Detector Integration Software, Madison, Wisconsin, USA, 2012.
- [18]. Bruker SADABS (Version 2004/1), Bruker AXS Inc., Area Detector Absorption Correction Software, Madison, Wisconsin, USA, 1998.
- [19]. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115-119.
- [20]. Farrugia, L. J.; WinGX, *J. Appl. Cryst.* **2012**, *45*, 849-854.
- [21]. Sheldrick, G. M.; SHELXL, *Acta Cryst. C* **2015**, *71*, 3-8.
- [22]. Brandenburg, K.; Putz, H. DIAMOND, Release 3.0e, Crystal Impact GbR, Bonn, Germany, 2006.
- [23]. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.