

Compound **2** crystallizes in monoclinic space group $C2/c$ with $a=11.697(3)$, $b=18.756(4)$, $c=8.549(4)$ Å, $\beta=94.50(1)^\circ$ and $Z=4$. In the binuclear molecule **1** (Figure) each Cd(II) cation is hexacoordinated in the N_3O_3 -environment in the shape of square bipyramid. Its basal plane is defined by a bidentate $NiOxH_2$ molecule and two monodentate acetate anions; water molecule and bidentate bpetha ligand occupy the apical sites, bpetha being coordinated to a symmetry-related metal atom in a bridge function and provides Cd–Cd separation of 13.86 Å. The water molecule in the apical position of the metal polyhedron demonstrates its cross-linking function being involved in hydrogen bonding with oxygen atoms of acetate anions via two $R_2^2(16)$ H-bonded cycles giving rise to the ordered layer where each binuclear unit is involved in 8 $OH\cdots O$ hydrogen bonds and is linked with four symmetry-related neighbors. The assembling of four molecules generates voids with the linear dimensions of ca. 11.16 x 22.24 Å, thus demonstrating the gradual increase in comparison with $[Cd_2(NiOxH_2)(bpy)(CH_3COO)_4(H_2O)_2]$ (where $bpy=4,4'$ -bipyridine) [1], where the voids have dimensions of ca. 11.12 x 20.47 Å.

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Keywords: cadmium compounds, coordination compounds, single-crystal X-ray crystallography

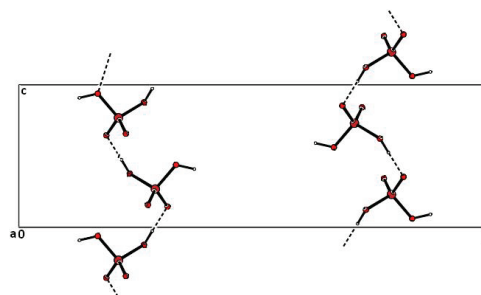
FA4-MS26-P13

Hydrogen-Bonding Graph-Set Motifs in p-Aminobenzoic Acid Derivatives. Amani Direm, Nourredine Benali-Cherif, *Laboratoire des Structures, Propriétés et Interactions Inter Atomiques (LASPPA). Centre Universitaire de Khenchela, Algérie*
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The present work is devoted to the analysis and the comparison of hydrogen-bonding graphs in crystal structures of six previously studied p-aminobenzoic acid salts : p-Carboxyanilinium dihydrogenphosphate (I) [1], p-Carboxyanilinium hydrogensulfate (II) [2], p-carboxyphenylammonium dihydrogenmonophosphate monohydrate (III) [3], bis (p-carboxyphenylammonium) sulfate (IV), p-carboxyphenylammonium perchlorate monohydrate (V) and p-carboxyphenylammonium nitrate (VI) [4].

These structures are dominated by N–H...O and O–H...O hydrogen bonding networks between the p-carboxyphenylammonium cations and the ionic molecules. O–H...O interactions between anions are present in the dihydrogenphosphate derivatives (I) and (III) giving rise to a $C_2^2(8)$ infinite chains. While intermolecular cation-cation H-bonds are only observed in the three compounds (IV), (V) and (VI).

The first-level graph set [5] of these compounds contains only D descriptors. Furthermore, the dihydrogenphosphate anions in (I) self-assemble to form supramolecular $C(4)$ chains along the c direction (see Figure below). While, the high-level graph sets of all six structures comprise essentially ring and chain motifs.



The $C(4)$ chain motifs running parallel to the $[001]$ direction.

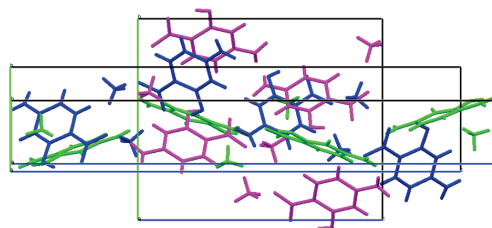
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Keywords: p-Aminobenzoic acid salts, H-bonds, Graph sets

FA4-MS26-P14

Polymorphic salts of the antibiotic 4-aminosalicylic acid. M. Teresa Duarte,^{a*} Vânia André,^a Dario Braga,^b Fabrizia Grepioni,^c *Centro de Química Estrutural, DEQB, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal,* ^b*Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy*
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4-aminosalicylic acid (ASA) is an antibiotic used in the treatment of tuberculosis. ASA has also shown to be safe and effective in the treatment of inflammatory bowel diseases [1]. Solvates, molecular salts and cocrystals of ASA have recently been disclosed and fully characterized by our group, using 6-membered non-aromatic rings, such as dioxane, morpholine and piperazin [2] or bigger cyclic compounds, such as 4,4'-bipyridine and DABCO [3] as crystal cofomers. Furthermore, studies on salt formation were conducted and three polymorphic ammonia salts of ASA have been synthesized and characterized. Different synthetic routes and methods lead to different final forms: liquid-assisted grinding and gas-solid diffusion yield pure polymorphic form II while the forms obtained by solution techniques are highly dependent on solvent and solution preparation conditions. These crystal forms are also obtained using slurry technique. The crystal structures of the three forms were determined and further characterization has been performed by XRPD, DSC, TGA and HSM.



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Keywords: Polymorphism, salts, 4-aminosalicylic acid

FA4-MS26-P15

Red $[K(2,2,2\text{-crypt})]_2[\{Ta_6\}Cl_{18}]$ featuring the 14-electron $\{Ta_6\}$ cluster. Katrin Dücker, Gerd Meyer, *Department für Chemie, Universität zu Köln, Germany*

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In its lower oxidation states, tantalum—like niobium—forms 16-electron octahedral clusters as for example in $K_4[\{Ta_6\}Cl_{18}]$ [1]. These compounds can be dissolved in a variety of solvents to form green solutions. Oxygen or other oxidizing agents transform these via a two-electron oxidation to red solutions [2].

To our surprise, red rhombic crystals emerged after two days at 4°C from a green solution of $K_4[\{Ta_6\}Cl_{18}]$ in an ethanol/dimethyl-sulfoxide mixture to which a solution of 2,2,2-crypt in ethanol had been added. The only obvious oxidizing agent could be oxygen from air. The single crystal structure determination exhibited the red crystals having the composition $[K(2,2,2\text{-crypt})]_2[\{Ta_6\}Cl_{18}]$ and crystallize in the triclinic space group $P\bar{1}$ with $a = 1105,1(2)$, $b = 1264,4(2)$, $c = 1379,5(3)$ pm, $\alpha = 107,95(1)$, $\beta = 90,64(1)$, $\gamma = 102,21(1)^\circ$.

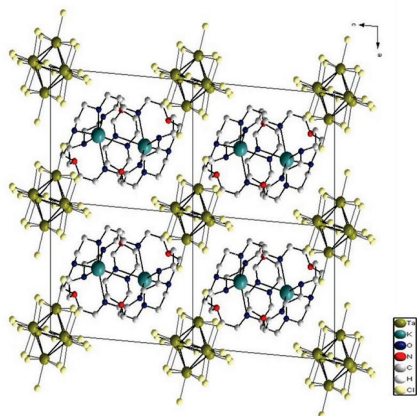


Fig 1. Projection of the crystal structure of $[K(2,2,2\text{-crypt})]_2[\{Ta_6\}Cl_{18}]$ down $[010]$.

The crystal structure of $[K(2,2,2\text{-crypt})]_2[\{Ta_6\}Cl_{18}]$ contains large cations which consist of K^+ ions encapsulated in the cryptand (2,2,2-crypt) and $[\{Ta_6\}Cl_{18}]^{2-}$ anions with a 14-electron $\{Ta_6\}$ cluster. The Ta—Ta distances along the twelve edges of the $\{Ta_6\}$ octahedron are around 299 pm (with little deviation) and are thus longer than those observed in $K_4[\{Ta_6\}Cl_{18}]$ which are around 290 pm. This expansion of the cluster is the result of the two-electron oxidation of $[\{Ta_6\}Cl_{18}]^{4-}$ (green) to $[\{Ta_6\}Cl_{18}]^{2-}$ (red).

Although examples of cluster complexes crystallized with cations employing coronands or cryptands are scarce, it is remarkable that with niobium, a 15-electron cluster could be isolated, for example in $[(H_2O_2)(18\text{-crown-6})_2]_3[\{Nb_6\}Cl_{18}]$ [3].

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Keywords: Cluster, Tantalum, Crown ether

FA4-MS26-P16

Pressure enhancement of $CH\cdots O$ interactions in simple ethers. Damian Jeczmiński, Kamil F. Dziubek, Andrzej Katrusiak, *Faculty of Chemistry, Adam Mickiewicz University Poznań, Poland*
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$CH\cdots O$ interactions attract attention of crystallographers, chemists and biochemists, although their importance was accepted widespread only in the last years of 20th century [1]. Despite their inherent weakness (typical potential energy < 4 kJ/mol), the topology of electron density redistribution accompanying the H-bond formation is similar to that of conventional hydrogen bonds [2]. Spectroscopic studies revealed that under high pressure $CH\cdots O$ interactions are enhanced and convert from van der Waals-like to hydrogen bonds [3]. We have recently supported this view with structural data.

Two simple ethers, tetrahydrofuran (THF) and its open-ring analogue diethyl ether (DE) have been chosen for the experiments to avoid masking $CH\cdots O$ interactions by stronger hydrogen bonds or Coulombic forces. For THF both isochoric crystallization at 2.25, 3.26, and 3.80 GPa and isobaric freezing at ambient pressure lead to a monoclinic phase, space group $C2/c$ [4]. The $CH\cdots O$ interactions are the strongest intermolecular forces in the THF molecular crystal, and the hierarchy of the $CH\cdots O$ distances correlates with the electrostatic potential distribution on a molecular surface and with their alignment along the lone pair direction. In THF the exposed oxygen atom is involved in six short $CH\cdots O$ contacts, a number highly unlikely for any strong hydrogen bonds. At high pressure all these interactions evolve into hydrogen bonds, and therefore the structure is stable to at least 3.80 GPa.

At low temperature DE crystallizes in the space group $P2_12_1$, $Z = 8$ (α -DE) [5]. The structure is fairly loosely packed, and each oxygen atom of two symmetry-independent molecules is involved in three $CH\cdots O$ contacts shorter than 3 Å. At high pressure DE solidifies below 1.9 GPa, yielding a new polymorph β -DE; space group $P2_1/c$, $Z = 4$, where three short intermolecular $CH\cdots O$ contacts per molecule are formed. Between 1.9 and 3.7 GPa DE undergoes a phase transition to the triclinic phase γ -DE; space group $P\bar{1}$, $Z = 2$. In γ -DE molecule adopts a *trans-gauche* conformation, contrary to the *trans-trans* conformation in both α -DE and β -DE phases. The energetic cost of transformation to a less stable conformation is compensated by facilitating the access to oxygen atom and hence the number of $CH\cdots O$ contacts increases to six per molecule.

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