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Keywords: Polymorphism, salts, 4-aminosalicylic acid

FA4-MS26-P15

Red [K(2,2,2-crypt)]₂[Ta₆Cl₁₈] featuring the 14-electron {Ta₆} 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 K₄[Ta₆Cl₁₈] [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 K₄[Ta₆Cl₁₈] 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-crypt)]₂[Ta₆Cl₁₈] and crystallize in the triclinic space group *P1* with *a* = 1105,1(2), *b* = 1264,4(2), *c* = 1379,5(3) pm, *α* = 107,95(1), *β* = 90,64(1), *γ* = 102,21(1)°.

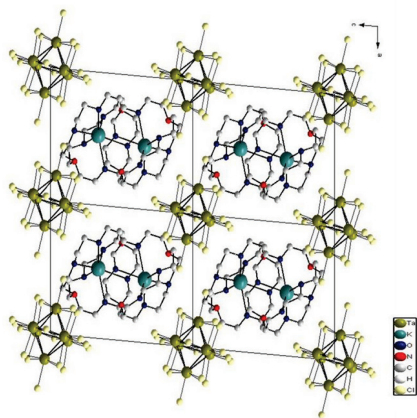


Fig 1. Projection of the crystal structure of [K(2,2,2-crypt)]₂[Ta₆Cl₁₈] down [010].

The crystal structure of [K(2,2,2-crypt)]₂[Ta₆Cl₁₈] contains large cations which consist of K⁺ ions encapsulated in the cryptand (2,2,2-crypt) and [Ta₆Cl₁₈]²⁻ anions with a 14-electron {Ta₆} cluster. The Ta—Ta distances along the twelve edges of the {Ta₆} octahedron are around 299 pm (with little deviation) and are thus longer than those observed in K₄[Ta₆Cl₁₈] which are around 290 pm. This expansion of the cluster is the result of the two-electron oxidation of [Ta₆Cl₁₈]⁴⁻ (green) to [Ta₆Cl₁₈]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 [(H₂O)₂(18-crown-6)₂]₃[Nb₆Cl₁₈] [3].

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FA4-MS26-P16

Pressure enhancement of CH···O interactions in simple ethers. Damian Jęczyński, Kamil F. Dziubek, Andrzej Katrusiak, *Faculty of Chemistry, Adam Mickiewicz University Poznań, Poland*
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CH···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···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···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···O interactions are the strongest intermolecular forces in the THF molecular crystal, and the hierarchy of the CH···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···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 *P2₁2₁2₁*, *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···O contacts shorter than 3 Å. At high pressure DE solidifies below 1.9 GPa, yielding a new polymorph *β*-DE; space group *P2₁/c*, *Z* = 4, where three short intermolecular CH···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 *P1*, *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···O contacts increases to six per molecule.

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Keywords: weak interactions, hydrogen bonds, high-pressure crystallography

FA4-MS26-P17

Hydrogen bonding and π - π stacking interactions in some important triheterocycles. Mukesh M. Jotani^a,

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The synthesis of triheterocycles, e.g. tetrazolopyrrolopyrimidine derivatives, involves various nucleophilic displacement reactions, such as chlorination, azidolysis and amination, on fused pyrimidines. Phase Transfer Catalysis (PTC), an environmentally benign technique, offers many advantages over conventional methodologies: viz. use of non-polar solvents, reduced reaction time and temperature, suppression of side-products, high-yields, replacement of hard bases, facile work-up, etc. Generally, the amination of 4-chloroazines requires harsh reaction conditions while fused tetrazolopyrimidine possess latent amino functionality giving facile amination, making these synthetic routes non-viable. However, the reductive ring cleavage of tetrazolo [1,5-c] pyrrolo [3,2-e] pyrimidines results in the formation of 4-aminopyrrolo[2,3-a] pyrimidines, which are of direct relevance to the pharmaceutical industry as synthetic precursors for more complicated molecules. Moreover, such compounds are found to possess a wide spectrum of biological activity. In view of the above, crystallographic studies of four such methoxy- and halogen-substituted 4-aminopyrrolo[2,3-a] pyrimidine derivatives were performed using single crystal X-ray diffraction techniques. The presence of various crystal packing interactions, and their influence on molecular structure, are supported by semi-empirical Quantum Chemical Calculations, using MOPAC2009 programme. Key results from the combined crystallographic and theoretical studies will be presented.

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Keywords: Hydrogen bonds, X-ray crystallography, Semi-empirical calculations

FA4-MS26-P18

The Influence of Substituent Variation and Packing Forces on the Conformation of Biphenyl Derivatives.

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The conformation of biphenyl derivatives has been the subject of a number of crystallographic investigations in the past [1 – 3]. In this contribution we report the crystal structures of two novel compounds, methyl 4-methoxy-2-nitrobiphenyl carboxylate and 4',4'-methoxy-2-nitrobiphenyl. The torsion angles about the central C-C bond are 50.5° and 57.4° respectively. These values are within the range observed in the Cambridge Structural Database (version 5.31, november 2009) [4] for similarly substituted biphenyl derivatives. An analysis of the packing in the crystals and molecular modeling will be used to discuss the difference in torsion angles.

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Keywords: conformations, biphenyl derivatives, single-crystal X-ray diffraction

FA4-MS26-P19

A modulated cocrystal:

N'-(propan-2-ylidene)nicotinohydrazide and sebacic acid. H. Krüger^a, V. Kahlenberg^a, A. Lemmerer^b and J. Bernstein^b, ^aInstitute of Mineralogy and Petrography, University of Innsbruck, Austria, ^bDepartment of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel

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Trying to cocrystallise nicotinic acid hydrazide (niazid) with sebacic acid from an acetone solution, resulted in a reaction of the niazid with the solvent. Cocrystals were formed, which contain molecules of *N'*-(propan-2-ylidene)nicotinohydrazide (*p*-niazid) and sebacic acid [1]. These cocrystals exhibit an incommensurately modulated structure. Structural analysis was performed using single-crystal X-ray diffraction data, collected at 173 K. After solution and refinement of the average structure (which includes disorder of the sebacic acid molecule) the modulated structure was refined using the (3+1)-dimensional superspace approach [2]. The structure belongs to the planar monoclinic crystal system ($a=5.07$, $b=44.51$, $c=6.40\text{Å}$, $\beta=94.6^\circ$, $\mathbf{q}=(-0.08, 0, 0.26)$) and the superspace group was determined to be $P2_1/n(a0\gamma)00$. Harmonic modulation functions of first order were successively introduced for all atom positions, but refined for non-hydrogen atoms only. The positions and modulation functions of the hydrogen atoms were fixed due to geometrical constraints. The final refinement included harmonic modulation waves for coordinates and ADPs for all non-hydrogen atoms. The *p*-niazid molecule, as well as the carboxylic groups of the sebacic acid are not much affected by the modulation, whereas the atoms of the hydrocarbon chain of the acid show a strong coordinated displacive modulation. The plane of the C-C bonds exhibits a rotation of up to 45° about the centre line of the ribbon. The crystal structure shows slabs packed with sebacic acid. These layers are oriented perpendicular to *b* and the sebacic acid molecules are tilted about 54° against *b*. We assume that weak intermolecular interactions within the sebacic acid layers cause the aperiodic