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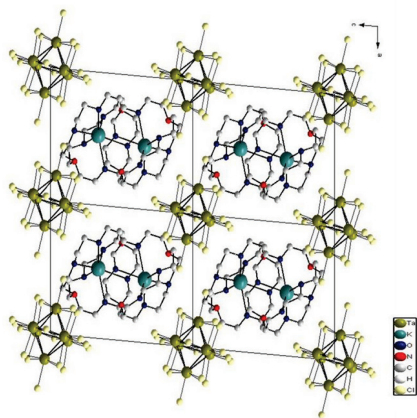
#### FA4-MS26-P15

**Red [K(2,2,2-crypt)]<sub>2</sub>[Ta<sub>6</sub>Cl<sub>18</sub>] featuring the 14-electron {Ta<sub>6</sub>} 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<sub>4</sub>[Ta<sub>6</sub>Cl<sub>18</sub>] [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<sub>4</sub>[Ta<sub>6</sub>Cl<sub>18</sub>] 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)]<sub>2</sub>[Ta<sub>6</sub>Cl<sub>18</sub>] 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)]<sub>2</sub>[Ta<sub>6</sub>Cl<sub>18</sub>] down [010].

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

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**Keywords:** Cluster, Tantalum, Crown ether

#### 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 *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*, *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 *P2<sub>1</sub>/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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