

## КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF BIS[1-{(3,5-DIMETHYL-1H-PYRAZOL-1-YL)METHYL}-3,5-DIMETHYL-1H-PYRAZOL-2-IUM] HEXACHLOROURANATE(IV):  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$ J. M. Carretas<sup>1</sup>, J. Cui<sup>1</sup>, A. Cruz<sup>1</sup>, I. C. Santos<sup>1,2</sup>, J. Marçalo<sup>1</sup><sup>1</sup> Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Bobadela LRS, Portugal

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The X-ray diffraction study of a single crystal with the composition  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$  (**1**) is performed. This compound is the product of an attempted synthesis of a bis(pyrazolyl)methane complex of uranium(IV) obtained by the reaction of  $\text{UCl}_4$  with bis(3,5-dimethylpyrazol-1-yl)methane in THF. **1** crystallizes in the space group *P*-1 of the triclinic system:  $a = 9.6616(2) \text{ \AA}$ ,  $b = 9.6946(2) \text{ \AA}$ ,  $c = 10.7314(2) \text{ \AA}$ ,  $\alpha = 107.6210(10)^\circ$ ,  $\beta = 115.5600(10)^\circ$ ,  $\gamma = 99.6710(10)^\circ$ ,  $V = 810.45(3) \text{ \AA}^3$ ,  $Z = 1$ ,  $d_{\text{calc}} = 1.765 \text{ g/cm}^3$ ,  $\mu = 5.528 \text{ mm}^{-1}$ ,  $R_1 = 0.0249$ . The structural unit consists of two separated  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]^+$  cations and a  $\text{UCl}_6^{2-}$  anion. In the solid state structure of **1** several short intermolecular  $\text{N}\cdots\text{H}\cdots\text{N}$  and  $\text{C}\cdots\text{H}\cdots\text{Cl}$  contacts are identified suggesting the presence of hydrogen bonds.

**Keywords:** uranium, bis(3,5-dimethylpyrazol-1-yl)methane, pyrazolium, crystal structure, short contacts.

The anionic tris(pyrazolyl)borate (Tp) ligands have been used with success as supporting ligands in the molecular chemistry of the *f*-block elements, actinides in particular [1–7]. These ligands provide an efficient protection of the metallic center and the possibility of tuning the steric and electronic properties of the complexes through the introduction of substituents in the pyrazolyl groups. Tris(pyrazolyl)methanes (Tpm) are the neutral, isoelectronic analogues of the Tp ligands and are part of the extended family of pyrazolylalkanes. We have recently reported the first synthesis and characterization of tris(3,5-dimethylpyrazol-1-yl)methane (Tpm\*) complexes of uranium(III, IV) and thorium(IV) [8], therefore extending the first reports [9, 10] with this type of ligands to the actinide series. As a part of our research in this area we decided to study bis(3,5-dimethylpyrazol-1-yl)methane (Bpm\*) complexes of uranium, and here we report the crystal structure of  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$  complex (**1**).

**Experimental.** The addition of a Bpm\* solution [11] (109 mg, 0.5 mmol) in THF to a  $\text{UCl}_4$  solution [12] (200 mg, 0.5 mmol) in the same solvent at room temperature resulted after stirring overnight in a green suspension. After centrifugation and removal of the solvent under vacuum the solid was washed with *n*-hexane and dried until dryness to give a green solid. Diffraction quality crystals were obtained from a THF/*n*-hexane solution at  $-5^\circ\text{C}$ .

Crystals of **1** suitable for the X-ray diffraction study were mounted on a loop with protective oil. X-ray data were collected at 150 K on a Bruker APEX II CCD diffractometer using graphite monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ) at 50 kV and 30 mA. Cell parameters were retrieved using the Bruker SMART [13] software and refined using Bruker SAINT [14] on all observed reflections.

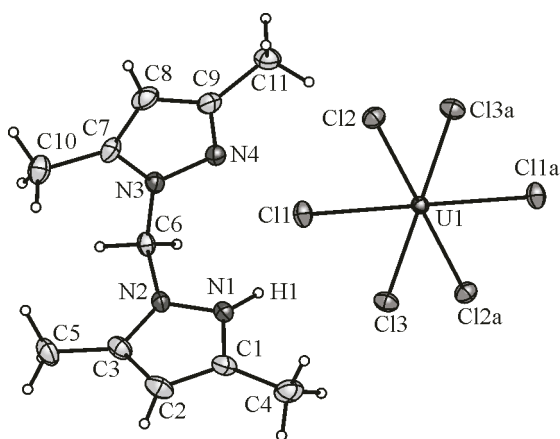


Fig. 1. ORTEP diagram of the  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]^+$  cation and the  $[\text{UCl}_6]^-$  anion units of  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$  **1**, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40 % probability level. [Symmetry codes: (a)  $x+1, y, z$ ]

Absorption corrections were applied using SADABS [15]. The structure solution and refinement were performed using direct methods with SIR97 [16] and SHELXL97 programs [17], both included in the WINGX-Version 1.80.05 package of programs [18]. A full-matrix least-squares refinement was used for the non-hydrogen atoms with anisotropic thermal parameters. All hydrogen atoms were inserted in ideal-

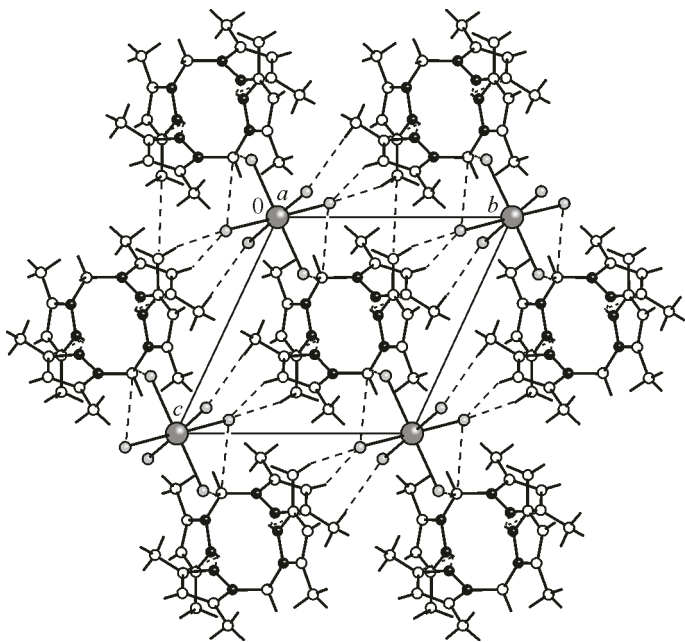
ized positions and allowed to refine riding on the parent carbon atom. The molecular structures were drawn with ORTEP3 for Windows [19].

Data for the compound have been deposited with CCDC under the deposit number 952776 and can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Crystallographic data for compound **1**:  $\text{C}_{22}\text{H}_{34}\text{N}_8\text{Cl}_6\text{U}$ ; green crystal (0.16×0.08×0.06 mm),  $M = 861.30$  g, triclinic, space group  $P-1$ ,  $a = 9.6616(2)$  Å,  $b = 9.6946(2)$  Å,  $c = 10.7314$  Å,  $\alpha = 107.6210(10)^\circ$ ,  $\beta = 115.5600(10)^\circ$ ,  $\gamma = 99.6710(10)^\circ$ ,  $V = 810.45(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $T = 150(2)$  K,  $d_{\text{calc}} = 1.765$  g/cm<sup>3</sup>,  $\mu = 5.528$  mm<sup>-1</sup>,  $F(000) = 416$ . Out of 7294 reflections collected, 3066 were independent ( $R_{\text{int}} = 0.030$ ); 177 parameters were refined with 3066 reflections to final  $R$  indices  $R_1$  ( $I > 2\sigma(I)$ ) = 0.0249,  $wR_2$  ( $I > 2\sigma(I)$ ) = 0.0535,  $R_1$  (all data) = 0.0251,  $wR_2$  (all data) = 0.0536, GOOF = 1.043.

**Results and discussion.** The reaction of bis(3,5-dimethylpyrazol-1-yl)methane with  $\text{UCl}_4$  in THF was studied and led to a product which could not be fully characterized. The elemental analysis data revealed a solid to be not completely pure, and no solvable NMR spectrum could be obtained. Nevertheless, green single crystals suitable for X-ray crystallographic studies were obtained from a THF/hexane solution at  $-5^\circ\text{C}$ . Attempts to synthesize a bis(pyrazolyl)methane complex of uranium(IV) proved to be unsuccessful and resulted in  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$  complex (**1**).

The  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$  compound crystallises in the triclinic system, space



group  $P-1$ , with the asymmetric unit comprising one independent  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz}) \times (3,5\text{-Me}_2\text{pzH})]^+$  cation located in a general position and a half of the  $[\text{UCl}_6]^{2-}$  dianion with the uranium atom located on the inversion centre. The ORTEP view of compound **1** is shown in Fig. 1.

The crystal structure of **1** is formed by stacks along the  $a$  axis composed by pairs of centrosymmetrically related  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]^+$  cations. In the  $bc$  plane these stacks form parallel layers to the  $b$  axis isolated from each other by  $[\text{UCl}_6]^{2-}$  di-anions (Fig. 2). The structure is

Fig. 2. Crystal packing of  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz}) \times (3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$  viewed along the  $a$  axis, showing the intermolecular short contacts

dominated by several intermolecular interactions and short contacts (Table 1).

In the independent  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]^+$  cation, the N1 nitrogen atom is protonated and the N1—H1 bond distance is 0.92(6) Å. The  $\text{UCl}_6^{2-}$  anion in **1** exhibits a slightly distorted octahedral structure with U—Cl distances of 2.6113(9) (U1—Cl1), 2.6330(8) Å (U1—Cl3), and 2.6358(9) Å (U1—Cl2). The average value of 2.6267(9) Å is in good agreement with the values found for compounds containing  $\text{UCl}_6^{2-}$  anions [20–22]. In **1** the Cl1—U1—Cl2, Cl1—U1—Cl3, and Cl2—U1—Cl3 bond angles are 88.87(3) Å, 89.67(3) Å, and 90.58(3) Å respectively. Well-known hexachlorouranate(IV) has been crystallised with a variety of counteranions, including  $[\text{NMe}_4]^+$  [23],  $[\text{PPh}_3\text{Et}]^+$  [24],  $[\text{MeBu}_3\text{N}]^+$  [21],  $[\text{BuMeIm}]^+$  (Im = imidazolium) [21, 22],  $[\text{BuMe}_2\text{Im}]^+$  [21], and  $[\text{EtMeIm}]^+$  [25, 26].

In the solid state structure of **1**, short intermolecular contacts (H1···N4a is 1.87 Å) were identified between the protonated N1 nitrogen atom of one  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]^+$  cation and a non-protonated N4 nitrogen atom of a unit generated by the inversion centre ( $2-x, 1-y, 1-z$ ), forming a pair of  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]$  units as shown in Fig. 3. This structure also comprises several short H···Cl contacts (shown in Fig. 2) that can be attributed to H-bonds according to the classical definition, *i.e.* their contact distances lie below the van der Waals cut-off distance ( $r_{\text{H}}^w + r_{\text{Cl}}^w$ ) [27]. More precisely, there are four short contacts with H···Cl distances of less than 2.95 Å, the shortest of which is 2.789 Å. Two hydrogen atoms are from methyl groups, one hydrogen atom is from C—H of the pyrazolyl ring and another hydrogen atom is from  $\text{CH}_2$  near two nitrogen atoms. Hydrogen bond distances and angles of some N—H···N and C—H···Cl contacts in **1** are presented in Table 1. The hydrogen bonding was previously observed between the  $\text{UCl}_6^{2-}$  anion and various cations:  $[\text{MeBu}_3\text{N}]^+$  [21],  $[\text{BuMeIm}]^+$  [21, 22],  $[\text{BuMe}_2\text{Im}]^+$  [21], and  $[\text{EtMeIm}]^+$  [26].

To the best of our knowledge there are no reports of compounds containing the  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]^+$  cation and  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$  could also be considered the first example of an *f*-element compound involving the formation of a pyrazolium fragment.

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Table 1

Hydrogen bond distances (Å) and angles (deg.) in  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]_2[\text{UCl}_6]$

D—H···A	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle(\text{DHA})$
C4—H···Cl2	2.831	3.798(6)	169.12
C6—H···Cl1	2.789	3.768(5)	170.04
C8—H···Cl2	2.856	3.735(6)	154.34
C11—H···Cl3	2.938	3.900(5)	167.47
N1—H1···N4	1.872	2.734(6)	155.14

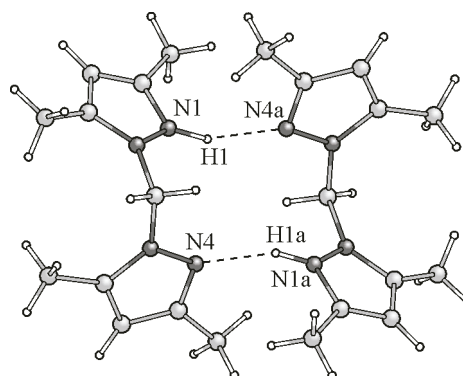


Fig. 3. Detail view of a centrosymmetrically related pair of  $[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})(3,5\text{-Me}_2\text{pzH})]^+$  cations emphasizing the N—H···N short contacts

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