



The “periodic table” of benzotriazoles: Uranium(VI) complexes[☆]



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ARTICLE INFO

Article history:

Received 22 May 2015

Received in revised form 26 June 2015

Accepted 29 June 2015

Available online 6 July 2015

Keywords:

Benzotriazoles

Crystal structures

Raman spectra

Uranyl complexes

ABSTRACT

The first employment of benzotriazoles in uranium(VI) chemistry has led to uranyl complexes with interesting structures and spectroscopic properties; the reactions of uranyl nitrate with 5,6-dimethylbenzotriazole give two products depending on the reactants' molar ratio.

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A popular class of ligands consists of azoles (e.g. pyrazoles and imidazoles), and one broad family of them are benzotriazole and its derivatives (Scheme 1). Over the last 30 years or so, we [1–8] and other groups [8–17] have been exploring the coordination chemistry of benzotriazoles. Research in this area ranges from efforts to model the corrosion inhibition of some metals (particularly Cu and its alloys) by benzotriazoles [18], to the synthesis of benzotriazolato coordination clusters [2,4–7,9,11,13,15] and polymers [1,3,12,14,16,17] with esthetically pleasing structures and exciting physical properties. Although the use of this family of ligands has been investigated widely in 3d- [1–11, 13–15,17] and 4f-metal [12,16] chemistry, their employment in the chemistry of 5f-metal ions has completely been ignored. We have been trying to create a “periodic table” of the benzotriazole-based ligands; we are now pleased to be able to fill in the empty 5f-metal position in this “periodic table” by describing the syntheses, structures and preliminary spectroscopic characterization of the first U(VI) complexes with benzotriazole-based ligation.

Interest in the coordination chemistry of the uranyl group (*trans* O=U=O) has recently increased for several reasons [19–22]. A basic understanding of this chemistry is very important for the selective complexation and separation of this ion from acid media during

reprocessing of irradiated advanced heavy water reactor (AHWR) nuclear fuel, nuclear plant effluents, seawater, and biological and environmental samples [23]. However, few UO_2^{2+} -simple azole complexes have been reported [24], and none is known with benzotriazoles as ligands.

Thus, we have decided to amalgamate the above mentioned research topics and to study reactions of uranyl nitrate with simple benzotriazole ligands; we report here our preliminary results in this area.

The reaction of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Mebta in a 1:2 molar ratio in MeCN at room temperature gave a yellow-green solution that upon storage at 20 °C produced yellowish green crystals of $[\text{UO}_2(\text{NO}_3)_2(\text{Mebta})_2]$ (**1**) in 40% yield. When an analogous reaction and crystallization was carried out by using 5MebtaH and diMebtaH, crystals of $[\text{UO}_2(\text{NO}_3)_2(6\text{MebtaH})_2]$ (**2**) and $[\text{UO}_2(\text{NO}_3)_2(\text{diMebtaH})_2]$ (**3**), respectively, were isolated in moderate to good yields. It is interesting to note that 5MebtaH tautomerizes into 6MebtaH ($\text{R}=\text{R}'=\text{H}$ and $\text{R}''=\text{Me}$ in Scheme 1) in complex **2**, i.e. upon coordination. A second product was isolated from the $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{diMebtaH}$ reaction system by employing an excess of the ligand. The reaction of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and diMebtaH in a 1:4 molar ratio in MeCN gave a dark brownish red solution that upon storage at 20 °C gave brown-yellow crystals of $[\text{UO}_2(\text{NO}_3)_2(\text{diMebtaH})_2] \cdot (\text{diMebtaH}) \cdot \text{MeCN}$ (**4** · diMebtaH · MeCN) in yields higher than 75%.

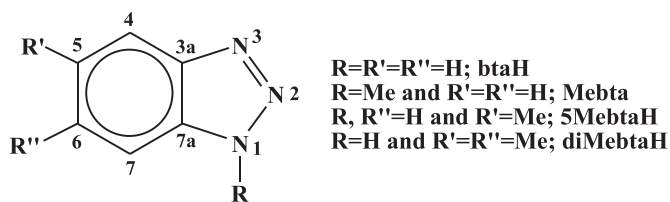
The structures of the four complexes were determined by single-crystal X-ray crystallography. The structures of the molecules $[\text{UO}_2(\text{NO}_3)_2 \text{L}_2]$ ($\text{L}=\text{Mebta}$, 6MebtaH, diMebtaH; Fig. 1) that are present in **1–3** and **4** · diMebtaH · MeCN present similarities and characteristic differences. Complex **2** contains two structurally similar, crystallographically independent $[\text{UO}_2(\text{NO}_3)_2(6\text{MebtaH})_2]$ molecules. The U^{VI} atoms

[☆] In memory of Paul Cordopatis: A great scientist, a fantastic mentor and a precious friend.

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Scheme 1. The general structural formula of benzotriazoles. The parent member of this family of ligands is 1H-benzo[d][1,2,3]triazole or simply benzotriazole (btaH; R=R'=R''=H). R, R' and R'' can be non-donor (Me, Cl, NO₂,...) or donor (OH, COOH, CH₂OH, CH₂COOH,...) groups. The ligands used and discussed in this work are 1-methylbenzotriazole (Mebta; R=Me, R'=R''=H), 5-methylbenzotriazole (5MebtaH; R'=Me, R=R''=H) and 5,6-dimethylbenzotriazole (diMebtaH; R'=R''=Me; R=H).

are at inversion centers in **1–3**, whereas no molecular symmetry elements are present in **4** · diMebtaH · MeCN. The gross molecular structure is common to all four complexes and show that each metal ion is surrounded by six oxygen and two nitrogen atoms in a hexagonal bipyramidal geometry. The two uranyl oxygen atoms occupy the axial positions. Four oxygen atoms of the two bidentate chelating nitrate groups, together with two nitrogen atoms of the neutral, planar monodentate benzotriazole ligands form the equatorial hexagonal plane. The U^{VI} and donor atoms in the equatorial plane are almost coplanar. The donor atom of Mebta, 6MebtaH and diMebtaH is the nitrogen atom of the position 3 of the azole ring (Scheme 1). The U=O bond lengths [1.734(5)–1.754(6) Å] are unremarkable [23], while the U–O_{nitrate} bond lengths are in the range 2.479(5)–2.529(5) Å with the nitrate N–O bond lengths being asymmetric due to coordination. The nitrate N–O_{coordinated} bond distances are in the range 1.251(10)–1.337(12) Å, with the N–O_{uncoordinated} bond distances in the range 1.206(8)–1.217(8) Å. The U–N_{benzotriazole} bond distances are between 2.507(5) and 2.551(7) Å.

The differences of the four complexes concern the relative orientations of the benzotriazole ligands. In compounds **1**, **2** and **3**, the benzene rings of the ligands are at opposite sides of the molecules (Fig. 1a, b, c, d),

whereas in the case of **4** (the molecule lacks a center of symmetry) the benzene rings of the two *trans* diMebtaH ligands are on the same side of the molecule (Fig. 1e). Another remarkable difference concerns the twist of the planes of the organic ligands relative to the planes of the coordinated nitrate groups. The dihedral angles between these planes are 86.9(3)° for **1**, 84.2(4)° for the U1-containing molecule of **2**, 68.7(3)° for the U2-containing molecule of **2**, 55.7(2)° for **3** and 74.8(2)°/84.4(2)° for **4**.

H bonds and π–π stacking interactions build the crystal structures of the four complexes. The most interesting crystal structure is that of **2** (Fig. 2), in which a 3D network is formed. The crystal structures of complexes **1**, **3** and **4** · diMebtaH · MeCN are shown in Figs. S1–S3 and full descriptions are provided in their legends.

The IR spectra of the complexes (Figs. S4–S7) show the existence of a strong band at 944 (**1**), 948 (**2**), 950 (**3**) and 934 (**4** · diMebtaH · MeCN) cm⁻¹ (not present in the spectra of the free ligands) assigned to the IR-active antisymmetric vibration of the {O=U=O}²⁺ group (ν₃) [25], which is red-shifted compared to the corresponding band for the aquo uranyl complexes (~965 cm⁻¹); this vibration does not appear in the Raman spectra of **1–3**, consistent with a centrosymmetric uranyl group in these complexes. The Raman-active uranyl symmetric stretch (ν₁) is observed at 855–865 cm⁻¹ in the Raman spectra (Fig. 3) and it is absent from the IR spectra of **1–3**. The non-centrosymmetric nature of the UO₂²⁺ group and the lattice diMebtaH's interaction with one uranyl oxo-oxygen atom in **4** · diMebtaH · MeCN are also corroborated using IR and Raman spectroscopies; the ν₃ and ν₁ vibrations appear in both the IR (934, 860 cm⁻¹) and Raman (930, 863 cm⁻¹) spectra (Fig. S8) of this complex [26].

The ¹H-NMR spectra (Figs. S9–S11) of the uranyl complexes **1**, **2** and **4** · diMebtaH · MeCN in d₆-DMSO reveal that these compounds decompose in solution to release the benzotriazole ligand; the spectra of the complexes are identical with those of the corresponding free ligands Mebta, 5MebtaH and diMebtaH, respectively. For example, the spectrum of **1** shows a sharp singlet at δ 4.30, a triplet at δ 7.39, a triplet at δ 7.55, a doublet at δ 7.83 and a doublet at δ 8.01 ppm, with relative

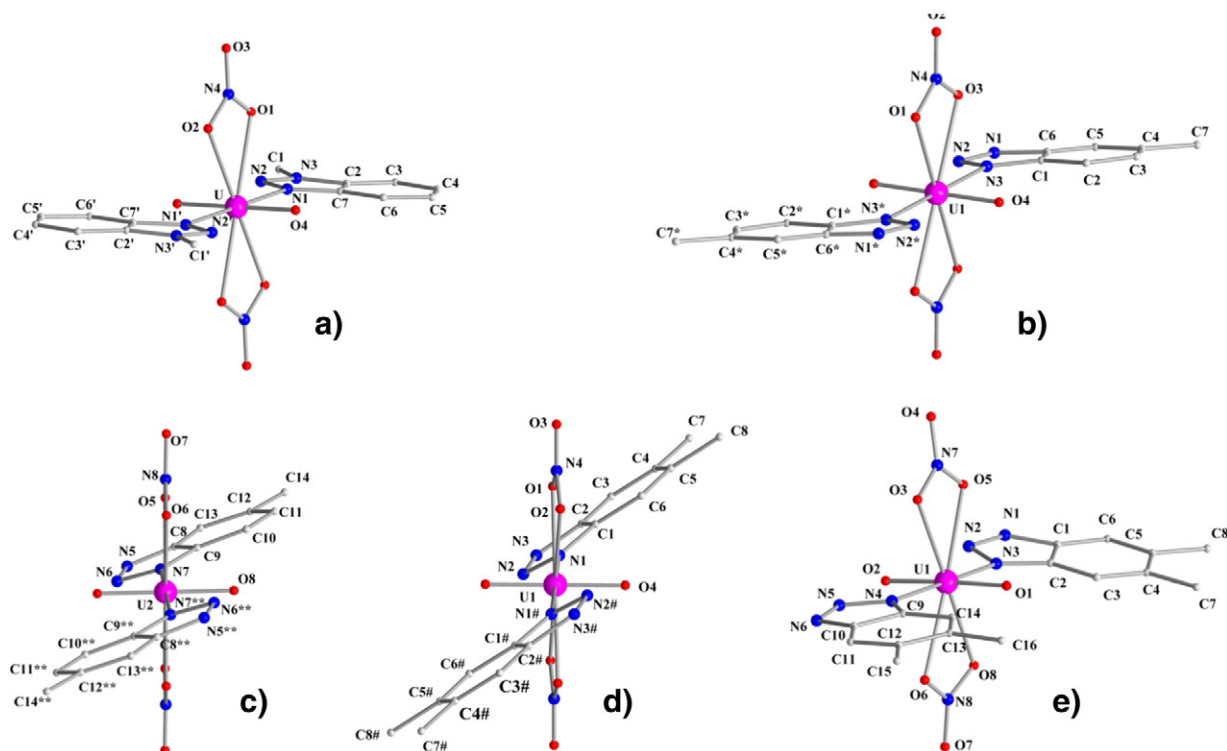


Fig. 1. Partially labeled plots of all the crystallographically independent molecules that are present in the structures of complexes **1** (a), **2** (b and c), **3** (d) and **4** (e). H atoms have been omitted. Symmetry codes ('): 1 - x, 1 - y, -z; (*): 1 - x, 1 - y, 1 - z; and (**, #): -x, 1 - y, -z. Symmetry-related uranyl oxido atoms and nitrate ligands have not been labeled.

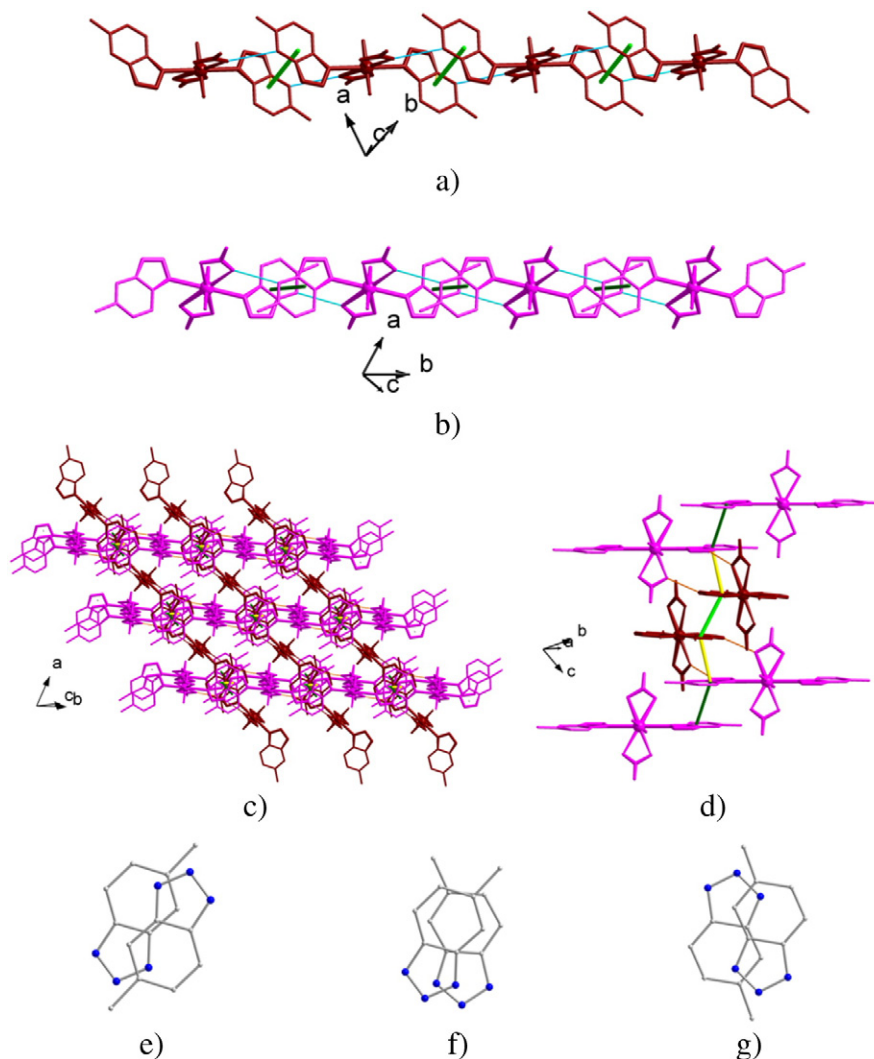


Fig. 2. a) The U1-containing molecules form chains through intermolecular π - π (light green lines) and "non-classical" H-bonding interactions ($C5-H5 \cdots O3$, Table S2, thin cyan lines), extended parallel to the $[1-10]$ crystallographic direction in the crystal structure of complex **2**. b) The U2-containing molecules form chains through intermolecular π - π (dark green lines) and "non-classical" H-bonding interactions ($C13-H13 \cdots O6$, Table S2, thin cyan lines), extended parallel to the b axis. These chains cross each other at points above and below the 6MehtaH ligands creating the 3D structure shown in c and resulting in stacks of ligands presented in d. Light green, yellow and dark green thick lines indicate the three different types of π - π overlaps in the structure of the complex, shown in e, f and g, respectively, with the corresponding distances and angles between the planes being 3.50 Å and 0° (e), 3.37 Å and 5.5° (f), and 3.44 Å and 0° (g). In the cases of e and g, the ligands are centrosymmetrically related.

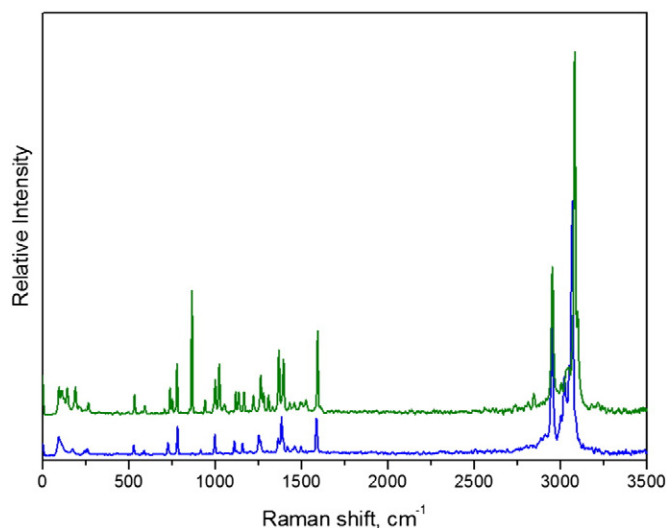


Fig. 3. The Raman spectra of Mehta (blue, bottom) and $[UO_2(NO_3)_2(Mehta)_2]$ (**1**).

integrations of 3:1:1:1:1, assigned to the methyl protons and the protons of the position 6, 5, 7 and 4 of the benzene ring, respectively [27]. There is evidence of the retainment of the structure of **3** in d_6 -DMSO based on the appearance of two singlets at δ 7.51 and 7.76 ppm (as opposed to the presence of one singlet peak at δ 7.64 ppm in the free ligand diMehtaH) assigned to the protons of the positions 7 and 4, respectively (Scheme 1).

In conclusion, we have developed access to the first members of the family of solid uranyl complexes with benzotriazole-based ligands. The products have interesting structures and spectroscopic features. Work in progress reveals that employment of benzotriazoles bearing – in addition to nitrogen – other donor groups (e.g. $R=OH$ and $R'=COOH$ in Scheme 1) delivers dinuclear and polynuclear U(VI) complexes that have novel topologies and interesting properties.

Appendix A. Supplementary data

Crystallographic data for **1**, **2**, **3** and **4** · diMehtaH · MeCN have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336 033; e-mail:

deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk> and may be obtained free of charge on quoting deposition numbers CCDC 1402399 (1), 1402402 (2), 1402400 (3) and 1402401 (4), respectively. Supplementary data with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.inoche.2015>.

References

- [1] K. Skorda, E.G. Bakalbassis, J. Mronzinski, S.P. Perlepes, C.P. Raptopoulou, A. Terzis, J. Chem. Soc. Dalton Trans. (1995) 2317–2319.
- [2] V. Tangoulis, C.P. Raptopoulou, A. Terzis, E.G. Bakalbassis, E. Diamantopoulou, S.P. Perlepes, Inorg. Chem. 37 (1998) 3142–3153.
- [3] V. Tangoulis, C.P. Raptopoulou, V. Psycharis, A. Terzis, K. Skorda, S.P. Perlepes, O. Cador, O. Kahn, E.G. Bakalbassis, Inorg. Chem. 39 (2000) 2522–2529.
- [4] G.S. Papaefstathiou, R. Vicente, C.P. Raptopoulou, A. Terzis, A. Escuer, S.P. Perlepes, Eur. J. Inorg. Chem. (2002) 2488–2493.
- [5] E. Diamantopoulou, C.P. Raptopoulou, A. Terzis, V. Tangoulis, S.P. Perlepes, Polyhedron 21 (2002) 2117–2126.
- [6] C. Papapatriantafyllopoulou, E. Diamantopoulou, A. Terzis, V. Tangoulis, N. Lalioti, S.P. Perlepes, Polyhedron 28 (2009) 1903–1911.
- [7] C. Gkioni, V. Psycharis, C.P. Raptopoulou, Polyhedron 28 (2009) 3425–3430.
- [8] N.C. Anastasiadis, G. Bilis, J.C. Plakatouras, C.P. Raptopoulou, V. Psycharis, C. Beavers, S.J. Teat, M. Louloudi, S.P. Perlepes, Polyhedron 64 (2013) 189–202.
- [9] M. Murrie, D. Collison, C.D. Garner, M. Helliwell, P.A. Tasker, S.S. Turner, Polyhedron 17 (1998) 3031–3043.
- [10] B.J. O'Keefe, P.J. Steel, Inorg. Chem. Commun. 3 (2000) 473–475.
- [11] L.F. Jones, E.K. Brechin, D. Collison, J. Raftery, S.J. Teat, Inorg. Chem. 42 (2003) 6971–6973.
- [12] K. Müller-Buschbaum, Y. Mokaddem, Eur. J. Inorg. Chem. (2006) 2000–2010.
- [13] R.H. Laye, Q. Wei, P.V. Mason, M. Shanmugam, S.J. Teat, E.K. Brechin, D. Collison, E.J.L. McInnes, J. Am. Chem. Soc. 128 (2006) 9020–9021.
- [14] X.-M. Zhang, Z.-M. Hao, W.-X. Zhang, X.-M. Chen, Angew. Chem. Int. Ed. 46 (2007) 3456–3459.
- [15] S. Biswas, M. Tonigold, M. Speldrich, P. Kögerler, M. Weil, D. Volkmer, Inorg. Chem. 49 (2010) 7424–7434.
- [16] J.C. Rybak, K. Müller-Buschbaum, Z. Anorg. Allg. Chem. 636 (2010) 126–131.
- [17] Y.-W. Li, K.-H. He, X.-H. Bu, J. Mater. Chem. A 1 (2013) 4186–4189.
- [18] A. Kokalj, S. Peljhan, M. Finšgar, I. Milošev, J. Am. Chem. Soc. 132 (2010) 16657–16668.
- [19] S. Fortier, T.W. Hayton, Coord. Chem. Rev. 254 (2010) 197–214.
- [20] S. Beer, O.B. Berryman, D. Ajami, J. Rebek Jr., Chem. Sci. 1 (2010) 43–47.
- [21] T. Loiseau, I. Mihalcea, N. Henry, C. Volkringer, Coord. Chem. Rev. 266–267 (2014) 69–109.
- [22] S.P. Kelley, P.S. Barber, P.H.K. Mullins, R.D. Rogers, Chem. Commun. 50 (2014) 12504.
- [23] B.G. Vats, S. Kannan, I.C. Pius, D.M. Noronha, D.K. Maity, M.G.B. Drew, Polyhedron 75 (2014) 81–87 (and refs. cited therein).
- [24] For example see: T. Kawasaki, T. Nishimura, T. Kitazawa, Bull. Chem. Soc. Jpn. 83 (2010) 1528–1530.
- [25] M.J. Manos, M.G. Kanatzidis, J. Am. Chem. Soc. 134 (2012) 16441–16446.
- [26] T.S. Franczyk, K.R. Gzerwinski, K.N. Raymond, J. Am. Chem. Soc. 114 (1992) 8138–8146.
- [27] A.R. Katritzky, W. Kuzmierkiewicz, J.V. Greenhill, Recl. Trav. Chim. Pays-Bas 110 (1991) 369–373.