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Crystal structures and conformers of $CyMe_4$-BTBP

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Abstract. The crystal structure of new conformation of the $CyMe_4$-BTBP ligand (*ttc*) has been presented. The *ttt* conformer of this compound in a form of THF solvate has been also crystallized. The geometries of six possible conformations (*ttt*, *ttc*, *tct*, *tcc*, *ctc* and *ccc*) of the $CyMe_4$-BTBP ligand have been modeled in the gas phase and in solutions (MeOH and H_2O) by DFT calculations using B3LYP/6-31G(d,p) method. According to the calculations, in the three different media the conformers with *trans* orientation of the N atoms in the bipyridyl moiety are the most stable.

Key words: conformers • crystal structure • $CyMe_4$-BTBP • DFT calculations

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Introduction

Triazinylpyridine N-donor ligands have been recently extensively studied as convenient substances in extraction processes for the separation of actinides (III) from lanthanides(III) [1–3]. Among them the 6,6′-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo-1,2,4-triazin-3-yl)-2,2′-bipyridine compound, known as $CyMe_4$-BTBP, is one of the most promising agent. This compound acts as tetradentate chelating ligand to the metal ions. The crystal structure of $CyMe_4$-BTBP in the form of methanol solvate was reported a few years ago [1]. Besides this ligand, among compounds of BTBP type, only C2-BTBP is available in the Cambridge Structural Database [1]. The crystal structures of the complexes of $CyMe_4$-BTBP with some metal cations (i.e. Pr^{3+}, Eu^{3+}, Tb^{3+} and Pb^{2+}) have been presented recently [3–6]. In addition, some quantum mechanical calculations on the geometry of BTBP ligands and their metal complexes have also been performed [1, 7]. Structural studies on this type of heterocyclic ligands and their complexes are still interesting because they can help to understand the processes of metals complexation and separation.

In this work the new crystal structures for two conformers of $CyMe_4$-BTBP have been shown. In addition, the calculations on the geometries of six conformers of the ligand discussed were carried out.

Experimental and calculation details

Chemicals

The $CyMe_4$-BTBP compound was synthesized according to the published method [1]. All other chemicals were used as purchased from commercial sources.

Crystallization

A small portions of $CyMe_4$-BTBP (about 5 mg) were recrystallized from acetonitrile, methanol, ethanol and tetrahydrofuran solutions (2 mL each), giving yellow crystals after slow evaporation of solvents at room temperature within a few weeks.

X-ray crystallographic analysis and data collection

Selected crystallographic parameters and refinement details for both conformers of $CyMe_4$-BTBP are summarized in Table 1. X-ray diffraction data were collected at 100 K on an Agilent Technologies SuperNova (dual source) diffractometer equipped with EOS CCD detector. Suitable crystals of both forms were mounted within a nylon loop by means of Paratone-N cryoprotectant oil. The mirror-monochromated Cu$K\alpha$ radiation (λ = 1.54184 Å) from a micro-focus Nova X-ray source was used for measurements. Data collection, data reduction and multi-scan absorption corrections were performed using CrysAlis PRO software. The structures were solved by direct methods and refined by full matrix least-squares method on F^2 data. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms bonded to carbon atoms were inserted into calculated positions with isotropic factors using riding model. The $CyMe_4$-BTBP ligand in structure **2** (see Table 1) exhibits a partial disorder in one tetramethylcyclohexane end of the molecule, with the refined ratio of two components being 0.68(1) : 0.32(1). There is also a strong disorder of the THF part in **2** showing two possible positions of that molecule with the occupancy rate refined to 0.58(1). All calculations were performed with the SHELXTL program package [8]. SHELXTL and MERCURY [9] programs were applied to prepare the crystal graphics.

The crystallographic data for this paper are deposited at the Cambridge Crystallographic Data Center (CCDC-1403274 (for **1**) and -1403275 (for **2**)). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Computational methodology

The calculations were performed using the Gaussian program [10]. Geometry optimization for the six

Table 1. Crystallographic data and structure refinement parameters for two conformers of $CyMe_4$-BTBP

Compound	$CyMe_4$-BTBP (**1**)	$CyMe_4$-BTBP·THF (**2**)
Empirical formula	$C_{32}H_{38}N_8$	$C_{36}H_{44}N_8O$
Formula weight	534.70	604.79
Temperature [K]	100(2)	100(2)
λ [Cu$K\alpha$] [Å]	1.54184	1.54184
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions:		
a [Å]	10.1131(2)	12.06128(10)
b [Å]	11.9272(3)	14.64799(13)
c [Å]	12.0979(3)	18.99678(18)
α [°]	80.7933(18)	90.00
β [°]	86.2899(17)	99.1300(8)
γ [°]	87.2089(17)	90.00
Volume [Å]	1436.35(5)	3356.22(5)
Z	2	4
Calculated density, D_c [g·cm^{-3}]	1.236	1.197
Absorption coefficient, μ [mm^{-1}]	0.597	0.590
F (000)	572	1296
Crystal size [mm]	0.22 × 0.18 × 0.10	0.24 × 0.12 × 0.10
Absorption correction	Multi-scan	Multi-scan
Transmission, T_{min}/T_{max}	0.6001/1.0000	0.79275/1.0000
Reflections collected	79702	56849
Independent reflections	5239	6027
R_{int}	0.0449	0.0280
Data/restraints/parameters	5239/0/369	6027/0/471
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0348 wR_2 = 0.0946	R_1 = 0.0525 wR_2 = 0.1381
GOF (F^2)	1.013	1.045
Largest difference peak/hole [e·Å^{-3}]	0.273/–0.201	0.637/–0.500

Table 2. Selected bond lengths, distances and torsion angles for the $CyMe_4$-BTBP conformers on the basis of calculated (for MeOH solutions) and experimental molecular structure (for all conformers the same labelling of atoms as in Figs. 1 and 2 were used)

	ttt	*ttt*	*ttc*	*ttc*	*ctc*	*tct*	*tcc*	*ccc*
	Calc.	Exp.	Calc.	Exp.	Calc.	Calc.	Calc.	Calc.
Bond lengths								
N1-C5	1.341	1.344(2)	1.341	1.339(1)	1.340	1.342	1.341	1.331
N2-C6	1.341	1.342(2)	1.340	1.340(1)	1.340	1.342	1.341	1.341
C1-C6	1.493	1.487(2)	1.492	1.494(1)	1.493	1.496	1.496	1.496
N5-N7	1.328	1.339(2)	1.328	1.335(1)	1.331	1.328	1.328	1.331
N6-N8	1.328	1.339(2)	1.330	1.338(1)	1.331	1.329	1.331	1.331
Distances								
N1···N2	3.610	3.599(2)	3.608	3.598(1)	3.607	2.827	2.795	2.806
N1···N3	2.756	2.761(2)	2.754	2.764(1)	3.621	2.763	2.752	3.620
N1···N5	3.609	3.574(2)	3.609	3.600(1)	2.740	3.603	3.607	2.745
N2···N4	2.756	2.751(2)	3.622	3.591(1)	3.621	2.766	3.622	3.620
N2···N6	3.609	3.575(2)	2.742	2.722(1)	2.740	2.599	2.743	2.746
Torsion angles								
N1-C5-C6-N2	–179.89	178.8(1)	179.85	–171.82(9)	180.00	–37.86	–33.16	–34.88
N1-C1-C22-N5	179.15	–165.7(1)	–177.85	–172.53(9)	–0.26	169.62	175.26	–7.14
N2-C10-C11-N6	179.15	162.3(1)	0.67	–21.30(1)	0.26	167.33	–2.24	–7.50

$CyMe_4$-BTBP conformers were performed at the DFT level by using the B3LYP functional combined with the 6-31G(d,p) basis set for both the gas phase and solutions (methanol and water) simulated using the Integral Equation Formalism Polarizable Continuum Model [11, 12]. No imaginary frequency was found for the studied structures confirming that all the conformers were true minima at potential energy surfaces. Relative energies given in Table 3 refer to the Gibbs free energies. The PCM approach was used only to qualitatively check whether the condensed media can significantly influence the conformation or not.

Results and discussion

Crystal structure studies

During our studies $CyMe_4$-BTBP was recrystallized from chosen solutions (see experimental part), giving yellow crystals after slow evaporation of solvents at room temperature within a few weeks. It appeared during single crystal X-ray pre-experiment that the same cell parameters were obtained for crystals precipitated from acetonitrile and alcohol solutions, but different from those reported earlier for the $CyMe_4$-BTBP–methanol solvate (1 : 1) which crystallized in the $P2_1/n$ space group [1]. Subsequent structure measurements found out a new conformer of $CyMe_4$-BTBP which crystallizes without any solvent molecule in the $P\bar{1}$ space group in the *ttc* conformation (Fig. 1). The arrangement of nitrogen atoms in four aromatic rings in $CyMe_4$-BTBP·MeOH indicated the presence of the *ttt* conformation [1]. In turn, the crystals obtained from THF solution gave the $CyMe_4$-BTBP–THF solvate (1 : 1) with the same space group and conformation as that for its methanol analogue (Fig. 2). For comparison, the C2-BTBP ligand adopts the *ctc* form in the solid state [1]. The conformation of the tetradentate ligand in both structures presented herein can be described by the three torsion angles formed between aromatic

Table 3. Relative energies [kJ/mol] of $CyMe_4$-BTBP conformations calculated in the gas phase and two solutions (the energies are expressed relative to the *ttt* conformer)

Conformer	Gas phase	MeOH	H_2O
ttt	0.00	0.00	0.00
ttc	2.82	–0.40	2.33
ctc	6.34	1.70	4.76
tct	29.15	21.32	20.72
tcc	32.27	19.89	20.00
ccc	41.66	26.19	23.62

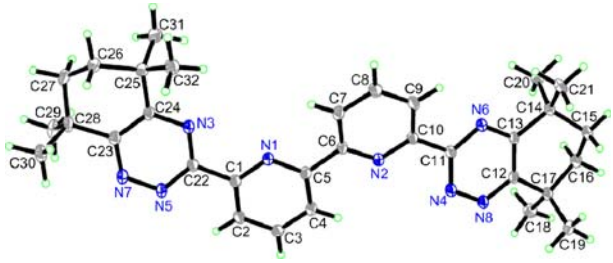

Fig. 1. Molecular structure of $CyMe_4$-BTBP (**1**) with the atom numbering scheme. The non-hydrogen atoms are shown as the 50% probability displacement ellipsoids.

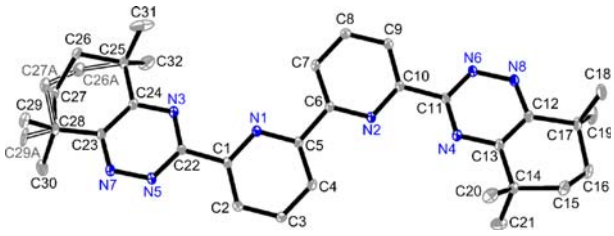

Fig. 2. Molecular structure of $CyMe_4$-BTBP as that in its THF solvate (**2**) with the atom numbering scheme. The modeled disorder in the tetramethylcyclohexane part of ligand is shown. The atoms are plotted with the 25% probability displacement ellipsoids. Hydrogen atoms are omitted for clarity.

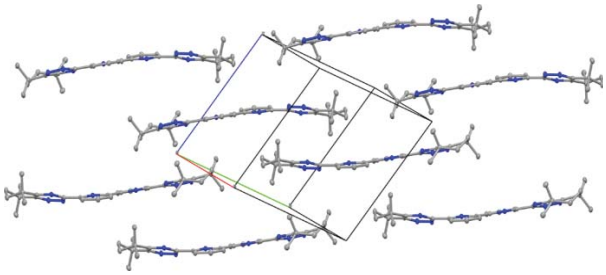

Fig. 3. The packing of the molecules of $CyMe_4$-BTBP (*ttc* conformer) in the unit cell of **1**.

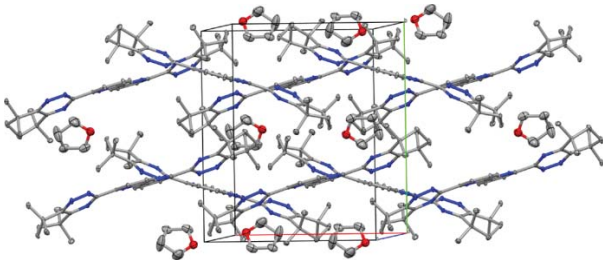

Fig. 4. The packing of the molecules of $CyMe_4$-BTBP (*ttt* conformer) and THF in the unit cell of **2**. The disorder of molecules is omitted for clarity.

rings. For the *ttc* conformer these torsion angles are equal to –171.82(9)° (N1-C5-C6-N2), –171.52(9)° (N1-C1-C22-N5) and –21.3(1)° (N2-C10-C11-N6) (see Table 2). In the case of *ttt* form, the corresponding torsion angles are 178.8(1), –165.7(1) and 162.3(1)°, respectively. The very similar values were obtained previously for *ttt* conformation in $CyMe_4$-BTBP·MeOH [1]. The packing of the $CyMe_4$-BTBP molecules in structure **1**, shown in Fig. 3, involves non-planar molecules of *ttc* conformer with the shortest C···C and C-H···N interatomic distances in the range 3.33–3.58 Å (C3···C20, 3.329(1) Å, C2-H2···N8, 3.386(1) Å, C31-H31C···N5, 3.448(1) Å, C3-H3···N6, 3.458(1) Å, C20-H20A···N6, 3.492(1) Å, C18-H18A···N5, 3.576(1) Å). The different molecular packing can be observed in the case of $CyMe_4$-BTBP·THF solvate (Fig. 4). The crystal structure of **2** is stabilized by the presence of the intermolecular hydrogen bonds of 3.290(2) Å (C9-H9···N5) and 3.370(2) Å (C2-H2···N6). In turn, the THF molecule forms only a very weak hydrogen-bonding interaction of 3.625(5) Å (O1···H26A-C26) with the neighbouring $CyMe_4$-BTBP ligand.

Computational studies

The geometries of six possible conformers (*ttt*, *ttc*, *ctc*, *tct*, *tcc* and *ccc*) of the $CyMe_4$-BTBP ligand in the gas phase and in water and methanol environments were modeled using DFT/IEF-PCM/B3LYP/6-31G(d,p) calculations (Table 3). The previous quantum mechanical calculations were carried out only for the BTBP-type ligand unsubstituted by alkyl groups (C0-BTBP) [1]. The selected bond lengths and distances calculated for the $CyMe_4$-BTBP conformers are presented in Table 2. For the *ttt* and *ttc* forms, the calculated geometrical parameters are in good agreement with those obtained from the crystal structure determination (Table 2). The Gibbs free energy values determined for all configurations indicate that the most stable in the presented media are three conformers with *trans* orientation of N atoms at the bipyridyl part (Table 3). The energies of these forms with a *trans* central torsion angle are lower than those with the *cis* angle by ca. 30 kJ/mol and 20 kJ/mol in the gas phase and in the two solvents, respectively. In the previous calculations performed for the C0-BTBP ligand [1], the analogous energy difference was found to be much smaller in solutions and greater in the gas phase. Nevertheless, one has to bear in mind that the present comparison between Gibbs free energies in the gas phase and in solvents is only a qualitative estimation of the effect of the condensed phase on conformation. Moreover, a more accurate approach requires adopting methodology described in [13].

Conclusions

The new crystal structures of two conformers of $CyMe_4$-BTBP ligand (*ttt* and *ttc*) have been obtained experimentally. The *ttc* conformer crystallized as a pure compound without any solvent molecule while the *ttt* form was found for the THF solvate. The calculations, carried out at the DFT/B3LYP/6-31G(d,p) level of theory, have shown that in chosen media among the six possible conformers of $CyMe_4$-BTBP compound the most stable are three forms with *trans* orientation of N atoms at the bipyridyl part (*ttt*, *ttc* and *ctc*). This seems to be in agreement with the experiments where two forms of this ligand have been obtained after crystallization process until now. In turn, the different behavior has been found for its complexes with metals ions for which the $CyMe_4$-BTBP molecule adopts the *ccc* conformation in order to bind to the metal [3–6].

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