Short Communication

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s-Block metal scorpionates – A new sodium hydrido-tris(3,5-dimethyl-1-pyrazolyl)borate salt showing an unusual core stabilized by bridging and terminal O-bonded DMSO ligands

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Abstract: Dissolution of $[(\mu\text{-Me}_2\text{CO})_3(\text{NaTp}^*)_2]$ (**1**) ($\text{Tp}^* = \text{hydrido-tris}(3,5\text{-dimethyl-1-pyrazolyl})\text{borate}$) in DMSO at room temperature leads to the growth of colourless crystals characterized as the new salt $[\text{Na}_2\text{Tp}^*(\mu\text{-Me}_2\text{SO})_3(\text{Me}_2\text{SO})_3][\text{NaTp}^*_2]$ (**2**). **2** crystallized in the trigonal space group $R\bar{3}$ with $Z=3$, $a=14.1227(2)\text{ \AA}$, $b=14.1227(10)\text{ \AA}$, $c=33.9685(2)\text{ \AA}$, and $V=5867.35(17)\text{ \AA}^3$. Interestingly, anion and cation of **2** both contain the Tp^* ligand. Moreover, the cationic moiety highlights an unusual sodium atom hexacoordinated by six DMSO molecules acting as O-bonded ligands. Three of which exhibit a bridging coordination mode and three are in terminal position. To the best of our knowledge, the framework of $[\text{Na}_2\text{Tp}^*(\mu\text{-Me}_2\text{SO})_3(\text{Me}_2\text{SO})_3]$ is unprecedented.

Keywords: hydrido-tris(3,5-dimethylpyrazol-1-yl)borate; sodium; DMSO coordination; crystal structure

1 Introduction

Since their discovery by Trofimenko (1967), coordination and organometallic chemistry of hydrido-tris(pyrazolyl)borate (Tp) ligands, also commonly named scorpionates, continues to arouse a great interest and creates new

prospects, especially in the field of medical imaging and therapy (Silva et al., 2017). From a structural point of view, although a large number of Tp metal complexes have been structurally elucidated, relatively few X-ray crystallographic characterization of derivatives of s-block metal have been published to date (Parkin, 1995). This is especially true for sodium derivatives for which we have only listed fifteen crystallographic reports deposited in the Cambridge Structural Database (CSD): $\{[\text{HB}(3\text{-CF}_3\text{-5-}\{4\text{-NO}_2\text{Ph}\}\text{Pz})_2(3\text{-}\{4\text{-NO}_2\text{Ph}\}\text{-5-CF}_3\text{Pz})]\text{Na}(\text{H}_2\text{O})\}_n$ (refcode: CUVCED) (van Dijkman et al., 2015) $\{[\text{HB}(3\text{-CF}_3\text{-5-}\{4\text{-CF}_3\text{Ph}\}\text{Pz})_2(3\text{-}\{4\text{-NO}_2\text{Ph}\}\text{-5-CF}_3\text{Pz})]\text{Na}_2(\mu\text{-H}_2\text{O})_2\}$ (refcode: CUVCIH) (van Dijkman et al., 2015), $[\text{HB}(3\text{-CF}_3\text{-5-Ph})\text{Pz}]\text{Na}(\text{THF})$ (refcode: ESUJUX) (Dias and Goh, 2004), $[\text{HB}(3\text{-CF}_3)_2\text{Pz}]\text{Na}(\text{OEt})$ (refcode: ESUKAE) (Dias et al., 2004), $[\text{HB}(3\text{-CF}_3)_2\text{Pz}]\text{Na}(\text{H}_2\text{O})$ (refcode: ESUKAI) (Dias and Goh, 2004), $\{[\text{HB}(3\text{-CF}_3)_2\text{Pz}]\text{Na}(\text{H}_2\text{O})\}_n$ (refcode: ESUKIM) (Dias and Goh, 2004), $[\text{Tp}_2\text{Bi}][\text{Tp}_2\text{Na}]\cdot 4\text{CH}_2\text{Cl}_2\cdot \text{Cl}(\text{CH}_2)_2\text{Cl}$ ($\text{Tm} = \text{hydrotris(methimazolyl)borate}$, $\text{Tp} = \text{hydrotris(pyrazolyl)borate}$) (refcode: HIXNEH) (Reglinski et al., 1999), $[\text{Na}_2(\text{Tp}^{\text{CF}_3, \text{INT}})_2(\mu\text{-acetone})_2]$ ($[\text{Tp}^{\text{CF}_3, \text{INT}}]^- = 3\text{-trifluoromethyl-5-(1-naphthyl)pyrazol-1-yl}]\text{borate}$) (refcode: IRECOZ) (van Dijkman et al., 2016), $[\text{HB}(3\text{-C}_2\text{F}_5)_2\text{Pz}]\text{Na}(\text{H}_2\text{O})$ (refcode: RAWXOC) (Dias and Kim, 1996), $\text{NaTp}^\#$ ($\text{Tp}^\# = \text{tris}[3\text{-}(2\text{-methoxy-1,1-dimethylethyl)pyrazolyl}]\text{hydroborate}$) (refcode: TEHSUV) (Chisholm et al., 2006, 2007), $[\text{HB}(3\text{-C}_2\text{F}_5)_2\text{Pz}]\text{Na}(\text{H}_2\text{O})$ (refcode: TUHMUF) (Hu et al., 2009), $\text{Tp}^{\text{n-C}_3\text{F}_7\text{Me}}\text{Na}(\text{THF})$ ($\text{Tp}^{\text{n-C}_3\text{F}_7\text{Me}} = \text{tris}(3\text{-}(1,1,2,2,3,3\text{-heptafluoropropyl})\text{-5-methyl-pyrazolyl})\text{borate}$) (refcode: TUJKAL) (King et al., 2009), $[\text{HB}(3,5\text{-CF}_3)_2\text{Pz}]\text{Na}(\text{H}_2\text{O})$ (refcode: ZUVQIQ) (Dias et al., 1996), $\{[\text{HB}(3\text{-CF}_3)_2\text{Pz}]\text{Na}(\text{THF})\}_2$ (refcode: ZUVQOW) (Dias et al., 1996). A few years ago, in the course of our studies on organotin(IV) scorpionates (Lange et al., 2016), we completed this inventory by reporting the X-ray crystal structure of $[(\text{Me}_2\text{CO})_3(\text{NaTp}^*)_2]$ (**1**) resulting from the treatment of

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Scheme 1: Molecular representations of $[(\mu\text{-Me}_2\text{CO})_3(\text{NaTp}^*)_2]$ (**1**) and $[\text{Na}_2\text{Tp}^*(\mu\text{-Me}_2\text{SO})_3(\text{Me}_2\text{SO})_3][\text{NaTp}^*_2]$ (**2**).

$\text{Tp}^*\text{Sn}(\text{Cl})_2\text{Bu}$ (Tp^* = hydridotris(3,5-methylpyrazolyl) borate) with NaOH in a mixture of acetone and water (Plasseraud and Cattey, 2014). The storage of the reaction medium at 4°C led to the formation of prismatic colourless crystals characterized as **1** (top of Scheme 1). In this contribution, we describe the recombination of **1** in the presence of dimethyl sulfoxide (DMSO) leading to the formation of the new salt **2**, whose the cationic component exhibits a hexacoordinated sodium atom with six O-bonded DMSO ligands (bottom of Scheme 1).

2 Results and discussion

The framework of **1** was described as two hydrido-tris(3,5-dimethyl-1-pyrazolyl)borate sodium moieties bridged by three acetone molecules acting as oxygen-based donors (Plasseraud and Cattey, 2014). When crystals of **1** are stored at 4°C in the crystallization solution, they remain stable several weeks. However at room temperature they gradually degrade. The thermogravimetric analysis performed on fresh crystalline sample of **1** demonstrated this relative fragility by showing a significant weight loss starting at relatively low temperature, from 70–75°C (Figure 1). This alteration can be explained by the facile breaking of the three bridges connecting the two sodium atoms and resulting from the release of the coordinated acetone molecules. The infrared spectrum recorded from crystals of **1** stored in an oven at 100°C during 1 h, corroborates this observation by clearly demonstrating

the complete disappearance of the carbonyl band (acetone ligands) located at 1698 cm^{-1} (Figures 2a,b). However as shown in the spectrum 1b, the other significant absorption bands are relatively unaffected, the C–H (pyrazole ring) and B–H elongations are still present around 3110 and 2450 cm^{-1} respectively. Moreover, the fingerprint in the range of 1600 to 500 cm^{-1} undergoes few changes, especially as regards the characteristic bands of the pyrazole ring and the B–N bond (Dehnicke and Fernández, 1976). Thus, this would imply the preservation of the Tp^* ligand.

Based on these observations and considering **1** as a promising reaction synthon, we investigated its reactivity toward molecules able to act as O-donor ligands with the aim to access to original frameworks of sodium scorpionates. Compound **1** is in particular well soluble in DMSO, tetrahydrofuran (THF), dimethyl ether (DME) and diethyl ether (Et_2O). Herein, we describe the result of the recombination of **1** in the presence of DMSO. The reaction was firstly monitored by ^1H NMR spectroscopy in $\text{DMSO}-d_6$. After several days at room temperature we observed the clear decrease in the intensity of the signal corresponding to the acetone ligands (Me_2CO) of **1** while Tp^* signals are still present (Figure 3). The same observation was made by $^{13}\text{C}\{^1\text{H}\}$ NMR while the ^{11}B spectrum did not show any differences (broad signal centred at –9 ppm).

Concomitantly colourless prismatic crystals grown at the bottom of the NMR tube. They were then characterized as being the new salt $[\text{Na}_2\text{Tp}^*(\mu\text{-Me}_2\text{SO})_3(\text{Me}_2\text{SO})_3][\text{NaTp}^*_2]$ (**2**). On the infrared spectrum of **2** (ATR analysis, Figure 2c), two absorption bands (weak) attributed to $\nu_{\text{B-H}}$ are observed at

Figure 1: TG-DTG analyses of **1** at a heating rate of $5^{\circ}\text{C min}^{-1}$ under nitrogen.

Figure 2: IR (ATR) spectra of (a) $[(\mu\text{-Me}_2\text{CO})_3(\text{NaTp}^*)_2]$ (**1**), (b) after storage of **1** for 1 h at 100°C , and (c) $[\text{Na}_2\text{Tp}^*(\mu\text{-Me}_2\text{SO})_3(\text{Me}_2\text{SO})_3][\text{NaTp}^*_2]$ (**2**).

2513 and 2252 cm^{-1} , which effectively support the presence of two distinct types of coordination for Tp^* ligands. However, no differentiation was possible in solution. Only one set of signals was observed for Tp^* by ^1H NMR spectroscopy. Compare to **1**, the IR spectrum is more abundant in the range

of $1100\text{--}950\text{ cm}^{-1}$, highlighting the presence of additional absorption bands (at 1051 and 1024 cm^{-1}) attributable to $\nu_{\text{S-O}}$ elongations and which supports the coordination of DMSO molecules (Calligaris, 2004). Furthermore, the CHN elemental analysis performed on crystals also supports

Figure 3: Time evolution of the ^1H NMR spectrum of **1** recorded in $\text{DMSO}-d_6$: (a) at the sample preparation, (b) after several days stored at room temperature.

the formula of **2**. Thus, the displacement of the acetone coordinating ligands of **1** by an excess of DMSO molecules and leading to **2**, can be summarized according to Equation 1. DMSO exhibits a higher Gutmann's donor number (DN) than acetone, $29.8 \text{ kcal}\cdot\text{mol}^{-1}$ against $17 \text{ kcal}\cdot\text{mol}^{-1}$ (Gutmann, 1976), which can be viewed as the driving force of the exchange, also supported by the reaction conditions (using a large excess of DMSO). DMSO molecule is known to show a high coordination ability. Thus, in recent decades and on several occasions, metal complexes with DMSO ligands were the subject of review articles focusing on structural aspects and coordination modes but also on their possible use in homogeneous catalysis (Alessio, 2004; Calligaris, 2004; Sipos et al., 2015).

An X-ray crystallographic analysis on suitable crystals of **2** confirmed the ionic structure of this new compound. Interestingly, the anionic and cationic components both incorporate Tp^*Na moieties. One free molecule of DMSO complete the unit cell of **2**. Crystallographic data and refinement details are summarized in Table 1. An ORTEP view, together with selected bonds lengths and angles, is shown in Figure 4. The $[\text{NaTp}^*]^-$ anion results on the hexacoordination of a sodium atom by two Tp^* ligands according to a sandwich-type structure. The sodium atom is in a distorted octahedral environment while Tp^* ligands adopt a propeller-like structure. The Na–N distances are in the range of $2.566(3)$ – $2.586(3) \text{ \AA}$. The N–Na–N intra ligand angles measure less than 90° [$\text{N3-Na3-N3} = 74.89(11)^\circ$].

Table 1: Crystal structure data for **2**.

Formula	$C_{27}H_{58}BN_6Na_2O_6S_6, C_{30}H_{44}B_2N_{12}Na, C_2H_6SO$
M_r	1507.44
T, K	100
Crystal system	trigonal
Space group	$R\bar{3}$
a , Å	14.1227(2)
b , Å	14.1227(10)
c , Å	33.9685(2)
α , deg	90
β , deg	90
γ , deg	120
V , Å ³	5867.35(17)
Z	3
$F(000)$, e	2412
D_{calcd} , g cm ⁻³	1.280
$\mu(\text{MoK}\alpha)$, mm ⁻¹	0.277
Crystal size, mm ³	$0.42 \times 0.40 \times 0.35$
hkl range	h : -18; 18 k : -18; 18 l : -44; 44
Diffractometer	Bruker APEX-II CCD
Scan Type	Mixture of ϕ rotations and ω scans
$((\sin\theta)/\lambda)_{\text{max}}$, Å ⁻¹	0.65
Refls. Collected	33252
Independent Refls.	5838
Refls. with $ I \geq 2\sigma(I)$	5776
R_{int}	0.0255
Refinement method	Full-matrix least-squares on F^2
Data / Restraints / Parameters	5838/1/308
R [$ I \geq 2\sigma(I)$]	$R1^a = 0.0331$, $wR2^b = 0.0833$
R (all data)	$R1^a = 0.0337$, $wR2^b = 0.0855$
Goodness of Fit (F^2) ^c	1.083
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.640 / -0.345

^a $R1 = \sum (|F_o| - |F_c|) / \sum |F_o|$; ^b $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + 1.9156P + (0.0615P)^2]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^c goodness of fit = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

while N–Na–N inter ligand angles are larger than 90° [N3–Na3–N5 = 103.67(10)°]. To our knowledge, this is only the second time that such a structure of a discrete anionic [NaTp₂][−] complex ion is described in the literature. The first example was reported by Reglinski et al. (1999) for the salt [Tm₂Bi][Tp₂Na] (Tm = hydrotris(methimazolyl)borate), isolated during the treatment of BiCl₃ by successive additions of NaTm, and then NaTp. More recently, a comparable arrangement for the anion was revealed by Bailey et al. (2001) in the hydrido-tris(thioxotriazolyl) borate (Tt) sodium salt [Tt₂Na]Na(H₂O)₆.

Regarding the cationic part of **2**, [Na₂Tp*(μ-Me₂SO)₃(Me₂SO)₃]⁺ consists of a dinuclear complex based

on two sodium atoms describing each distinct coordination environments. Na1 is coordinated by one Tp* ligand in an [N₃] mode [Na1–N = 2.459(3)] and by the oxygen atoms of three DMSO molecules acting as μ-O-bonded bridging ligands [Na1–O1 = 2.384(3), O1–S1 = 1.491(3) Å]. Na2 is also connected to these DMSO molecules [Na2–O1 = 2.373(3)] and its coordination sphere is completed by three supplementary molecules of DMSO, η-O-bonded [Na2–O2 = 2.486(3), O2–S2 = 1.512(3) Å]. Thus, the two sodium atoms are hexacoordinated, both describing distorted octahedral geometries. Values of N1–Na1–N1, O1–Na1–O1 and O1–Na2–O1 angles are less than 90°. The Na⋯Na distance measures 3.267(3) Å and is thus shorter than that observed for the starting compound **1** (Na⋯Na = 3.4697(7) Å). However, in case of **2**, this distance is very close to that determined in the polymeric compound [Na(C₃H₆O)₃]_n(I₂)_n (Na⋯Na = 3.2237(4) Å) isolated by addition of a saturated solution of NaI in acetone to a solution of HCl, SnCl₂ and H₂C=CHCO₂Me in diethyl ether (Howie and Wardell, 2003). In our opinion, the most remarkable structural feature of **2** resides in the coordination of the sodium atom Na2 by six molecules of DMSO. To the best of our knowledge, previously such a fragment has been only observed once (based on a CDS query), and attributed to the polymeric edifice [Na₄(DMSO)₁₅][I₃]₃(I) (refcodes: ITITAH, KAZWAM) (Duarte-Ruiz et al., 2011; Plata et al., 2017). Therefore, the structure of the cationic moiety [Na₂Tp*(μ-Me₂SO)₃(Me₂SO)₃]⁺ can be considered as unprecedented for a discrete complex.

From a supramolecular interest, a view of the crystalline packing of **2** is depicted in Figure 5. The organization can be considered as a columnar-like arrangement oriented along the c -axis. It is based on the alignment and the repetition of sequences involving a free molecule of DMSO, the cation [Na₂Tp*(μ-Me₂SO)₃(Me₂SO)₃]⁺ and the anion [NaTp₂][−]. In conclusion, a new sodium hydrido-tris(3,5-dimethyl-1-pyrazolyl)borate salt was elucidated describing, for both the anion and the cation, unusual structures. Other studies are in progress to extend the reactivity of compound **1** to other O-donor molecules.

Experimental

General

The starting compound [(μ-Me₂CO)₃(NaTp*)₂] (**1**) was synthesized according to a previous published method (Plasseraud and Cattey, 2014). The standard NMR spectra were recorded at 300 K in DMSO-*d*₆ on a Bruker Avance

Figure 4: ORTEP view of the molecular structure of $[\text{Na}_2\text{Tp}^*(\mu\text{-Me}_2\text{SO})_3(\text{Me}_2\text{SO})][\text{NaTp}^*]$ (2) with crystallographic numbering scheme (hydrogen atoms are omitted for clarity) (B yellow, N blue, O red, S yellow, C grey, Na turquoise). Selected bond lengths (Å) and angles (deg) with estimated standard deviations in parentheses: B1–N2 1.552(3), B2–N4 1.541(3), B3–N6 1.538(3), Na1–N1 2.459(3), Na3–N3 2.566(3), Na3–N5 2.586(3), Na1–O1 2.384(3), Na2–O1 2.373(3), Na2–O2 2.486(3), O1–S1 1.491(3), O2–S2 1.512(3), O3–S3 1.504(4), Na1...Na2 3.267(3); N2'–B1–N2'' 111.0(2), N1–N2–B1 122.1(3), Na2–O1–Na1 86.75(11), N2–N1–Na1 117.3(2), N1–Na1–N1'' 79.75(11), O1–Na1–N1' 169.17(14), O1–Na1–N1 108.73(12), O1'–Na1–N1 94.89(11), O1'–Na1–O1 77.81(12), O1'–Na2–O1 78.24(12), O1–Na2–O2 126.85(13), O1–Na2–O2'' 78.20(9), O1–Na2–O2' 140.24(14), O2–Na2–O2' 91.08(10), S1–O1–Na1 139.17(18), S1–O1–Na2 130.66(17), S2–O2–Na2, 112.78(16) [Symmetry Code: (i) $1-y, 1+x-y, +z$; (ii) $+y-x, 1-x, +z$; (iii) $1+y-x, 1-x, +z$; (iv) $1-y, +x-y, +z$].

Figure 5: MERCURY representation showing the crystal packing of **2** along the *c*-axis (hydrogen atoms are omitted for clarity).

300 spectrometer. ^1H and ^{13}C chemical shifts (δ , ppm) were determined from the residual solvent signal ($(\text{CH}_3)_2\text{SO}$ $\delta=2.50$, $(\text{CD}_3)_2\text{SO}$ $\delta=39.52$). ^{11}B NMR spectra were calibrated using $\text{BF}_3\cdot\text{Et}_2\text{O}$ as external reference. IR spectra were recorded on a Bruker Vector 22 (Wissenbourg, France) equipped with a Specac Golden GateTM ATR device. Thermogravimetric analyses (TGA) were performed on a TA Instruments TGA Q500 thermoanalyzer using aluminium pans. Samples were heated from room temperature to 600°C at a rate of 5°C min^{-1} under flowing nitrogen gas. The gas flow rate at the sample was $60\text{ mL}\cdot\text{min}^{-1}$, while the balance flow rate was $40\text{ mL}\cdot\text{min}^{-1}$. Elemental analyses were performed at the Institut de Chimie Moléculaire (Université de Bourgogne Franche-Comté, Dijon-France) using a Thermo Electron CHNS/O Flash EA 112 Series analyser.

Isolation of $[\text{Na}_2\text{Tp}^*(\mu\text{-Me}_2\text{SO})_3(\text{Me}_2\text{SO})_3][\text{NaTp}^*_2]$ (**2**)

Initially, the salt **2** was isolated by preparing an NMR tube based on a sample of **1** dissolved in $\text{DMSO-}d_6$ (Sigma-Aldrich). The storage of the sample in air and at room temperature led after several days to the growth of prismatic colourless single crystals which were characterized as **2**. The isolation of **2** as crystalline material was also obtained

in non-deuterated DMSO (30% yield). - IR (ATR, cm^{-1}): 3112 (w), 2948 (m), 2922 (m), 2861 (w), 2513 (m), 2252 (w), 1680 (w), 1539 (s), 1482 (w), 1436 (m), 1411 (s), 1373 (m), 1347 (s), 1193 (vs), 1137 (w), 1069 (s), 1050 (vs), 1024 (s), 1006 (s), 978 (m), 805 (s), 781 (s), 764 (vs), 697 (s), 666 (m), 650 (vs), 454 (s). - ^1H NMR (300.130 MHz, $\text{DMSO-}d_6$, 300 K): δ = 5.49 (s, 6H, 4-pz-CH), 4.68 (br, 2H, BH), 2.27 (s, 18H, pz- CH_3), 1.83 (s, 18H, pz- CH_3). - $^{13}\text{C}\{^1\text{H}\}$ NMR (75.467 MHz, $\text{DMSO-}d_6$, 300 K): 145.7 (pz-C CH_3), 141.4 (pz-C CH_3), 102.8 (pz-CH), 13.4 (pz-C CH_3), 12.9 (pz-C CH_3). - ^{11}B NMR (96.293 MHz, $\text{DMSO-}d_6$, 300 K): δ = -9.1 (br, BH). - Anal. Calcd for $\text{C}_{57}\text{H}_{102}\text{B}_3\text{N}_{18}\text{Na}_3\text{O}_6\text{S}_6\cdot(\text{CH}_3)_2\text{SO}$ ($1507.46\text{ g mol}^{-1}$): C 47.00, H 7.22, N 16.72. Found: C 47.01, H 7.20, N 17.72.

X-ray crystallography

A suitable single crystal of **2** was mounted on a mylar loop, and the diffraction data were collected at 100 K on a Bruker D8 Venture triumph Mo equipped with a nitrogen jet stream low-temperature system (Oxford Cryosystems). The X-ray source was graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073\text{ \AA}$) from a sealed tube. The total number of runs and images was based on the strategy calculation from the program APEX3 (Bruker, 2015) and the unit cell was refined using SAINT (Bruker, V8.34A, after 2013). Data reduction, scaling and absorption

corrections were performed using SAINT (Bruker, V8.34A, after 2013). A multi-scan absorption correction was performed using SADABS-2012/1 (Bruker, 2012) was used for absorption correction. Using OLEX2 (Dolomanov et al., 2009), the structure was solved by Intrinsic Phasing using the SHELXT program (Sheldrick, 2015) and refined with full-matrix least-squares on F^2 using the version 2018/3 of SHELXL program (Sheldrick, 2008, 2015). Programs used for the representation of the molecular and crystal structures: OLEX2 (Dolomanov et al., 2009), MERCURY (Macrae et al., 2008). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions and refined as riding atoms.

CCDC 1985584 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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