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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 \([\mu\text{-}Me_2CO]\)\((NaTp^*)_2\) \((1)\) (Tp* = hydrido-tris(3,5-dimethyl-1-pyrazolyl)borate) in DMSO at room temperature leads to the growth of colourless crystals characterized as the new salt \([Na_2Tp^* (\mu\text{-}Me_2S\text{O})_3 (Me_2S\text{O})_3][NaTp^*]^2\) \((2)\). 2 crystallized in the trigonal space group R3 with \(Z = 3\), \(a = 14.1227(2)\ \text{Å}\), \(b = 14.1227(10)\ \text{Å}\), \(c = 33.9685(2)\ \text{Å}\), and \(V = 5867.35(17)\ \text{Å}^3\). 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 \([Na_2Tp^* (\mu\text{-}Me_2S\text{O})_3 (Me_2S\text{O})_3][NaTp^*]^2\) 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): \([\text{HB}(3\text{-}CF_3\text{-}5-(4\text{-}NO_2\text{-}Ph})\text{Pz}_2(3\text{-}(4\text{-}NO_2\text{-}Ph)-5\text{-}CF_3\text{-}Pz)]\text{Na}(H_2O)\) \((\text{refcode: CUVCED})\) (van Dijkman et al., 2015), \([\text{HB}(3\text{-}CF_3\text{-}5-(4\text{-}CF_3\text{-}Ph})\text{Pz}_2(3\text{-}(4\text{-}NO_2\text{-}Ph)-5\text{-}CF_3\text{-}Pz)]\text{Na}_2(\mu\text{-}H_2O)_2\) \((\text{refcode: CUVCIH})\) (van Dijkman et al., 2015), \([\text{HB}(3\text{-}CF_3\text{-}5\text{-}(\text{Ph})\text{Pz})_3]\text{Na}(\text{THF})\) \((\text{refcode: ESUJUX})\) (Dias and Goh, 2004), \([\text{HB}(3\text{-}(\text{CF}_3\text{-}5\text{-}(\text{Ph}))\text{Pz})_2]\text{Na}(\text{OEt}_2)\) \((\text{refcode: ESUKAE})\) (Dias et al., 2004), \([\text{HB}(3\text{-}(\text{CF}_3\text{-}5\text{-}(\text{Ph}))\text{Pz})_3]\text{Na}(\text{THF})\) \((\text{refcode: ESUKEI})\) (Dias et al., 2004), \([\text{HB}(3\text{-}(\text{CF}_3\text{-}5\text{-}(\text{Ph}))\text{Pz})_3]\text{Na}(\text{H}_2\text{O})\) \((\text{refcode: CUVCH})\) \((\text{Dias and Goh, 2004})\), \([\text{HB}(3\text{-}(\text{CF}_3\text{-}5\text{-}(\text{Ph}))\text{Pz})_3]\text{Na}(\text{H}_2\text{O})\) \((\text{refcode: ESUKKE})\) (Dias and Goh, 2004), \([\text{TM}_2\text{Bi}][\text{TP}_2\text{Na}]\cdot 4\text{CH}_2\text{Cl}_2\cdot \text{Cl}(\text{CH}_2\text{Cl}_2)\) \((\text{refcode: HIXNEH})\) (Reglinski et al., 1999), \([\text{Na}(_{\text{TP}}\text{CF}_3\text{-}1\text{Nt})^2(\mu\text{-}acetone)]\) \((\text{TP}_{\text{CF}_3\text{-}1\text{Nt}}=\text{3-trifluoromethyl-5-(1-naphthyl)pyrazol-1-yl}^\text{borate})\) \((\text{refcode: IREC02})\) (van Dijkman et al., 2016), \([\text{HB}(3\text{-(C}_2\text{F}_5\text{-}5\text{-}(\text{CH}_3))\text{Pz})_3]^2\text{Na}(\text{THF})\) \((\text{refcode: RAWXOC})\) (Dias and Kim, 1996), NaTp* \((\text{Tp}^* = \text{tris}[3\text{-}(2\text{-}methoxy\text{-}1\text{-}dimethyl)\text{pyrazolyl}]^\text{borate})\) \((\text{refcode: TEHSUV})\) (Chisholm et al., 2006, 2007), \([\text{HB}(3\text{-}(\text{CF}_3\text{-}5\text{-}(\text{CH}_3))\text{Pz})_3][\text{Na}(\text{H}_2\text{O})]\) \((\text{refcode: ZUVQIQ})\) (Dias et al., 2006), \([\text{HB}(3\text{-}(\text{CF}_3\text{-}5\text{-}(\text{CH}_3))\text{Pz})_3]^2\text{Na}(\text{H}_2\text{O})\) \((\text{refcode: ZUVQOW})\) (Dias et al., 2006). 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 \([\text{Me}_2\text{CO}]\)\((\text{NaTp}^*)^2(1)\) resulting from the treatment of
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1 TP*Sn(Cl)2Bu (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 (Et2O). Herein, we describe the result of the recombination of 1 in the presence of DMSO. The reaction was firstly monitored by \(^1\)H NMR spectroscopy in 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 (\(\text{Me}_2\text{CO}\)) of 1 while TP* signals are still present (Figure 3). The same observation was made by \(^{13}\)C(\(^1\)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 [Na2TP*\(\mu\text{-}\text{Me}_2\text{SO}\),\(\text{Me}_2\text{SO}\)]\([\text{NaTP}^*\text{]2}\) (2). On the infrared spectrum of 2 (ATR analysis, Figure 2c), two absorption bands (weak) attributed to \(\nu\text{B–H}\) are observed at

### Scheme 1: Molecular representations of [(\(\mu\text{Me}_2\text{CO}\)),\(\text{NaTP}^*\)]\(2\) \((1)\) and [\(\text{Na}_2\text{TP}^*(\mu\text{-}\text{Me}_2\text{SO}),\text{Me}_2\text{SO}\)]\([\text{NaTP}^*\text{]2}\) \((2)\).
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 \(^1\)H NMR spectroscopy. Compare to 1, the IR spectrum is more abundant in the range of 1100–950 cm\(^{-1}\), highlighting the presence of additional absorption bands (at 1051 and 1024 cm\(^{-1}\)) attributable to \(v_{S=O}\) elongations and which supports the coordination of DMSO molecules (Calligaris, 2004). Furthermore, the CHN elemental analysis performed on crystals also supports
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 kcal·mol⁻¹ against 17 kcal·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 [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) Å. The N–Na–N intra ligand
angles measure less than 90° [N3–Na3–N3 = 74.89(11)°]

Figure 3: Time evolution of the ¹H NMR spectrum of 1 recorded in DMSO-d₆: (a) at the sample preparation, (b) after several days stored at
room temperature.
Table 1: Crystal structure data for 2.

| Parameter                      | Value                      |
|-------------------------------|----------------------------|
| Formula                       | \( C_{27}H_{58}BN_{6}Na_{2}O_{6}S_{6}, C_{30}H_{44}B_{2}N_{12}Na, C_{2}H_{6}SO \) |
| \( M_{r} \)                   | 1507.44                    |
| \( T, K \)                    | 100                        |
| Crystal system                | tridengonal                |
| Space group                   | \( R3 \)                   |
| \( a, \AA \)                  | 14.1227(2)                 |
| \( b, \AA \)                  | 14.1227(10)                |
| \( c, \AA \)                  | 33.9685(2)                 |
| \( \alpha, \deg \)            | 90                         |
| \( \beta, \deg \)             | 90                         |
| \( \gamma, \deg \)            | 120                        |
| \( V, \AA^3 \)                | 5867.35(17)                |
| \( Z \)                       | 3                          |
| \( F(000), e \)               | 2412                       |
| \( D_{\text{calc}}, \text{g cm}^{-3} \) | 1.280                      |
| \( \mu(\text{MoK}a), \text{mm}^{-1} \) | 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 f rotations and w scans |
| Refs.                         | 32352                      |
| Independent Refs.             | 5776                       |
| Refs. 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                 |
| \( R = \sum \frac{|F| - |F|}{|F|} \sum \frac{|F|}{|F|} \) | 0.0331, \( wR2^2 = 0.0833 \) |
| (all data)                    | \( R = \sum \frac{|F| - |F|}{|F|} \sum \frac{|F|}{|F|} \) | 0.0337, \( wR2^2 = 0.0855 \) |
| Goodness of Fit (\( F^2 \))   | 1.083                      |
| \( \Delta d_{\text{m}} \) (max/min, e \( \AA^{-3} \)) | 0.640 / -0.345 |

\( R1 = \sum \frac{|F| - |F|}{|F|} \sum \frac{|F|}{|F|} \) \( wR2 = \sum \frac{w(F_o^2 - F_c^2)}{w(F_o^2 + P)} \) where \( w = 1/[\sigma(F_o^2) + 1.9156P + 0.0615P^2] \) when \( P = \sum \frac{w(F_o^2 + P)}{2(F_o^2)} \); 
\( \Delta d_{\text{m}} \) goodness of fit = \( \sum \frac{w(F_o^2 - F_c^2)}{w(F_o^2 + P)} \). 

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 \([\text{NaTp}]^+\) complex ion is described in the literature. The first example was reported by Reglinski et al. (1999) for the salt \([\text{Tm}2\text{Bi}][\text{TpNa}]\) (\( \text{Tm} = \text{hydrotiris(methimazolyl)borate} \)), isolated during the treatment of \( \text{BiCl}_3 \) by successive additions of \( \text{NaTm} \), and then \( \text{NaTp} \). More recently, a comparable arrangement for the anion was revealed by Bailey et al. (2001) in the hydrido-tris(thioxotriaazolyl) borate (Ti) sodium salt \([\text{TiNa}][\text{Na(HO)}]_6 \).

Regarding the cationic part of 2, \([\text{Na}_2\text{Tp}(\mu-\text{Me}_2\text{SO})_2]_2\text{(Me}_2\text{SO})_2]_2^+\) consists of a dinuclear complex based on two sodium atoms describing each distinct coordination environments. \( \text{Na}_1 \) is coordinated by one \( \text{Tp}^* \) ligand in an \([N]_3 \) mode \([\text{Na}1-\text{N} = 2.459(3) \) \] and by the oxygen atoms of three \( \text{DMSO} \) molecules acting as \( \mu-O \)-bonded bridging ligands \([\text{Na}1-\text{O}1 = 2.384(3), \text{O}1-\text{S}1 = 1.491(3) \) \]. \( \text{Na}_2 \) is also connected to these \( \text{DMSO} \) molecules \([\text{Na}2-\text{O}2 = 2.486(3), \text{O}2-\text{S}2 = 1.512(3) \) \]. Thus, the two sodium atoms are hexacoordinated, both describing distorted octahedral geometries. Values of \( \text{N1}–\text{Na1}–\text{N1}, \text{O1}–\text{Na1}–\text{O1} \) and \( \text{O1}–\text{Na2}–\text{O1} \) angles are less than 90°. The \( \text{Na}–\text{Na} \) distance measures 3.267(3) \( \AA \) and is thus shorter than that observed for the starting compound 1 (\( \text{Na}–\text{Na} = 3.4697(7) \) \). However, in case of 2, this distance is very close to that determined in the polymeric compound \([\text{Na}(\text{C}_3\text{H}_6\text{O})_3]_n(\text{I}_2)_n \) (\( \text{Na}–\text{Na} = 3.2237(4) \) \) isolated by addition of a saturated solution of \( \text{NaI} \) in acetone to a solution of \( \text{HCl}, \text{SnCl}_2, \text{H}_2\text{C}–\text{CH}_2\text{Me} \) 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 \( \text{Na}_2 \) by six molecules of \( \text{DMSO} \). 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 \([\text{Na}(\text{DMSO})_6]_n(\text{I}_2)_n(\text{O}) \) (refcodes: ITITAH, KAZWAM) (Duarte-Ruiz et al., 2011; Plata et al., 2017). Therefore, the structure of the cationic moiety \([\text{Na}_2\text{Tp}(\mu-\text{Me}_2\text{SO})_2]_2\text{(Me}_2\text{SO})_2]_2^+\) 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 \( \text{DMSO} \), the cation \([\text{Na}_2\text{Tp}(\mu-\text{Me}_2\text{SO})_2]_2\text{(Me}_2\text{SO})_2]_2^+ \) and the anion \([\text{NaTp}]^+ \). 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 \([\mu-\text{Me}_2\text{CO}]_3\text{(NaTp)}]_2(\text{I})\) (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 \([\text{Na}_2\text{Tp}'(\mu-\text{Me}_2\text{SO})(\text{Me}_2\text{SO})][\text{NaTp}']\) (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–N1 111.0(2), N1–N2–B1 122.1(3), Na2–O1–Na1 86.75(11), N1–Na1–N1 79.75(11), O1–Na1–Na2 169.17(14), O1–Na1–N1 94.89(11), O1–N1–Na1 17.78(12), O1–Na2–O1 78.24(12), O1–Na2–O2 126.85(13), 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].
300 spectrometer. $^1$H and $^{13}$C chemical shifts ($\delta$, ppm) were determined from the residual solvent signal ((CH$_3$)$_2$SO $\delta$ = 2.50, (CD$_3$)$_2$SO $\delta$ = 39.52). $^{11}$B NMR spectra were calibrated using BF$_3$·Et$_2$O as external reference. IR spectra were recorded on a Bruker Vector 22 (Wissenbourg, France) equipped with a Specac Golden Gate™ 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 mL·min$^{-1}$, while the balance flow rate was 40 mL·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 [Na$_2$Tp*(μ-Me$_2$SO)$_3$(Me$_2$SO)$_3$][NaTp*$_2$] (2)**

Initially, the salt 2 was isolated by preparing an NMR tube based on a sample of 1 dissolved in 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 (w), 2250 (w), 1680 (w), 1539 (s), 1482 (w), 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), 545 (s). - $^1$H NMR (300.130 MHz, DMSO-$d_6$, 300 K): $\delta$ = 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$_3$). - $^{13}$C{1H} NMR (75.467 MHz, DMSO-$d_6$, 300 K): 145.7 (pz-CCH$_3$), 141.4 (pz-CCH$_3$), 102.8 (pz-CH), 13.4 (pz-CCH$_3$), 12.9 (pz-CCH$_3$). - $^{11}$B NMR (96.293 MHz, DMSO-$d_6$, 300 K): $\delta$ = -9.1 (br, BH). - Anal. Calcd for C$_{57}$H$_{102}$B$_3$N$_{18}$Na$_3$O$_6$S$_6$·(CH$_3$)$_2$SO (1507.46 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$_{\alpha}$ radiation ($\lambda = 0.71073$ Å) 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

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