A Novel Alkali-Metal Hydrido-tris(pyrazolyl)borate (Tp\(^{\ast}\)) Complex. Isolation and Crystal Structure of \([\text{Me}_2\text{CO}]_3\text{(NaTp}^{\ast}\text{)}_2\]}

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The title compound was isolated from the treatment of Tp\(^{\ast}\)Sn(Cl)\(_2\)Bu (1) with a large excess of sodium hydroxide in a mixture of acetone-water at room temperature. \([\text{Me}_2\text{CO}]_3\text{(NaTp}^{\ast}\text{)}_2\] (2) crystallizes at 4 °C as prismatic colorless crystals, in the monoclinic space group \(P2_1/c\) with \(Z = 4\), \(a = 12.2837\) (6), \(b = 24.3197\) (12), \(c = 16.9547\) (8) Å, \(\beta = 110.017(1)^\circ\), and \(V = 4759.0(4)\) Å\(^3\). The X-ray crystallographic analysis revealed a dinuclear unit in which two Tp\(^{\ast}\)Na moieties are held together by three bridging acetone molecules acting as oxygen-based donors.

Key words: Hydrido-tris(pyrazol-1-yl)borate, Tin, Sodium, X-Ray Crystallography

Introduction

Since their discovery by S. Trofimenko [1], the coordination and organometallic chemistry of hydrido-tris(pyrazolyl)borate ligands (Tp), also commonly called scorpionates, was intensively explored, with a great interest in particular for biomimetic applications [2]. Thus, a large number of structures of metal Tp complexes have been elucidated by X-ray crystallographic analysis [3 – 5]. From a synthetic point of view, the historic pathway to such compounds requires the use of alkali-metal precursors [6]. Interestingly, Tani and Mashima reported an alternative route showing that organotin complexes, in particular Tp\(^{\ast}\)Sn(Cl)\(_n\)Bu\(_{3-n}\), could be efficiently employed as reagents for the preparation of group 4 (Zr) and 5 (Nb, Ta) hydrido-tris(3,5-dimethylpyrazolyl)borates [7, 8]. Subsequently, this method was successfully applied by other research groups for the preparation of new transition metal [9 – 11] and rare earth pyrazolate derivatives [12].

In the course of our ongoing studies in the organotin(IV) chemistry, and aiming in particular to isolate new polynuclear entities containing Sn–O bonds [13 – 17], we have been led to study the reactivity of Tp\(^{\ast}\)Sn(Cl)\(_2\)Bu (1) with NaOH, in a mixture of acetone and water. Indeed, in the past this procedure was successfully applied by Roy and co-workers for the synthesis of diorganotin oxides from dichloride precursors [18]. However, applying this method to 1, unexpected prismatic colorless crystals were collected after storage of the solution at 4 °C. The X-ray crystallographic analysis performed on suitable crystals revealed the formation of a new sodium hydrido-tris(3,5-dimethylpyrazolyl)borate complex characterized as \([\text{Me}_2\text{CO}]_3\text{(NaTp}^{\ast}\text{)}_2\] (2). In this contribution, we describe the solid-state structural characterization of 2 which exhibits an unprecedented dimeric structure established via three bridging acetone molecules (Scheme 1).

Results and Discussion

When an acetone solution of Tp\(^{\ast}\)Sn(Cl)\(_2\)Bu (1) was treated with an aqueous solution of sodium hydroxide (1 : 12 mole ratio) at room temperature, the reaction mixture became biphasic after a few days. Stored at 4 °C, prismatic colorless crystals grew from the
upper phase. Preliminary IR (ATR) analysis revealed in particular the presence of characteristic stretching vibrations at 3108 and 2516 cm\(^{-1}\), matching with C–H (pyrazole ring) and B–H bonds of the Tp* ligand. However, compared to the IR fingerprint of 1 (Fig. 1a), notable modifications could be observed around 2800–3000 cm\(^{-1}\) (C–H stretching), and a distinct new strong absorption band located in the carbonyl stretching region at 1698 cm\(^{-1}\) (Fig. 1b).

An X-ray crystallographic analysis on suitable crystals solved unambiguously the structure 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 Fig. 2. Two hydrido-tris(3,5-dimethyl-1-pyrazolyl)borate sodium moieties are held together by three bridging acetone molecules acting as oxygen-based donors, corroborating the assignment of the intense IR band observed at 1698 cm\(^{-1}\). Each sodium atom is six-coordinated in a facial arrangement to three nitrogen atoms of the same Tp* ligand and to three oxygen atoms of the acetone molecules. The molecule belongs to
The pyrazole rings as well as the acetone planes exhibit a weak propeller-shaped orientation. The angles between the plane of the oxygen atoms and the six pyrazole planes are 85.68(4), 81.70(3), 88.63(4), 71.75(5), 83.96(3), and 83.70(4)°. In the past, a comparable arrangement was reported for (μ-aqua)(potassium hydrido-tris(4-chloro-3,5-dimethylpyrazol-1-yl)borate)2 [19]. A view along the Na⋯Na direction is shown in Fig. 3. The characterization of 2 was also completed by 1H, 13C[1H] and 11B NMR spectroscopy (all spectra are displayed in the Supporting Information available online; see note at the end of the paper for availability) and elemental analysis which confirm the results obtained by X-ray crystallography. Interestingly, the dinuclear structure of 2 is also preserved in CDCl3 solution as confirmed by the X-ray structure determined from single crystals collected in an NMR tube which proved to be 2·3CHCl3 (see Fig. S7 and Tables S8–S14 in the Supporting Information).

Surprisingly, only few solid-state structures of sodium hydrido-tris(pyrazolyl)borate complexes are known. To this date, nine crystallographic reports have been registered in the Cambridge Structural Database (CSD): [HB(3,5-(CF3)2Pz)3]Na(H2O) [20], [[HB(3-(CF3)Pz)3]Na(thf)]2 [20], [HB(3-(CF3), 5-(Ph)Pz)3]Na(thf) [21], [HB(3-(CF3),5-(Ph)Pz)3]Na(H2O)]n [21], [HB(3-(CF3)2Pz)3]Na(OEt2) [21], a slightly distorted D_{3h} point group.
of a structurally characterized sodium tris(pyrazolyl)borate, in which the coordination of both Na atoms by three bridging molecules of acetone is unusual. To the best of our knowledge, only three structures exhibiting this mode of coordination were previously reported in the literature (based on a CDS query): [Na₃(Me₂CO)₁₂][Pb₄I₁₃(Me₂CO)] [25], [Na(Me₂CO)₉]n (I₂)ₙ [26] and [Na₄((Me₂CO)₁₅)[PbI₂I₁₂·3Me₂CO)] [27]. The three examples include exclusively polynuclear cations consisting of a collinear array of Na atoms. Therefore, the dinuclear (Me₂CO)₉Na₂ core revealed in 2 can be considered as unprecedented. A comparison of the Na–O bond lengths, the Na–O–Na distances, and the Na–O–Na angles with related compounds is given in Table 2.

Parallel to these structural investigations and using ¹¹⁹Sn[¹¹H] NMR spectroscopy as an investigation tool, we sought to elucidate the nature of the tin-containing co-products. No signals were observed of the solution from which 2 had crystallized. However, the ¹¹⁹Sn[¹¹H] NMR spectrum measured in D₂O of the residue collected after the complete evaporation of the lower phase (strongly alkaline, pH = 14), revealed a predominant signal at −494 ppm (a minor signal is also observed at −588 ppm). Such a chemical shift can be attributed to a six-coordinated tin atom. In addition, the ¹H and ¹³C[¹¹H] NMR spectra showed exclusively the resonances characteristic of an n-butyl chain. ¹H, ¹³C[¹¹H], and ¹¹⁹Sn NMR spectra are pre-

Table 2. Comparison of Na–O bond lengths (Å), Na–Na distances (Å), and Na–O–Na angles (deg) in µ-acetone-Na complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Na–O (Å)</th>
<th>Na–O–Na (deg)</th>
<th>Na–Na (Å)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Na₃(Me₂CO)₁₂][Pb₄I₁₃(Me₂CO)]</td>
<td>2.457(11)–2.388(11)</td>
<td>89.3(3)</td>
<td>3.379(7)</td>
<td>[25]</td>
</tr>
<tr>
<td>[Na(Me₂CO)₉]n</td>
<td>2.439(5)</td>
<td>82.7(2)</td>
<td>3.2237(4)</td>
<td></td>
</tr>
<tr>
<td>[Na₄((Me₂CO)₁₅)[PbI₂I₁₂·3Me₂CO)]</td>
<td>2.457(11)–2.388(11)</td>
<td>89.3(3)</td>
<td>3.379(7)</td>
<td>[27]</td>
</tr>
<tr>
<td>Na₃[SnF₆]·C₂Ph₂I₂·3Me₂CO[(DMSO)]</td>
<td>2.492(7)–2.346(6)</td>
<td>99.3(2)</td>
<td>3.691(5)</td>
<td>[28]</td>
</tr>
<tr>
<td>[Na₂(LH)₂][Me₂CO]₁₂·2CHCl₃·2H₂O</td>
<td>2.394(5)–2.368(5)</td>
<td>108.2(2)</td>
<td>3.857(3)</td>
<td>[29]</td>
</tr>
<tr>
<td>(calix[4]arene)Na₂·Me₂CO</td>
<td>2.441(7)</td>
<td>106.9(4)</td>
<td>3.923(3)</td>
<td>[30]</td>
</tr>
<tr>
<td>[Na₉(Me₂CO)₁₄(OH)₁₃][I(FcSn)₃S₁₂]</td>
<td>2.316(6)–2.390(6)</td>
<td>110.6(2)</td>
<td>4.313(1)</td>
<td>[31]</td>
</tr>
<tr>
<td>[[Me₂CO]₉]NaTp⁺</td>
<td>2.4431(9)–2.4298(10)</td>
<td>91.29(3)</td>
<td>3.4697(7)</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>2.4064(10)–2.4094(9)</td>
<td>91.61(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.4095(10)–2.4126(11)</td>
<td>92.11(4)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a L = calix[4]arene; b this work.

Fig. 3 (color online). DIAMOND representation of 2 as seen along the Na–Na direction with H atoms omitted, and highlighting the pseudo-3 (C₃) symmetry (N blue, O red, C grey, B green, Na violet).

[[HB(3-(CF₃)₅-(CH₃)Pz)₃][Na(H₂O)]₂ [21], [Tm₂Bi] [Tp₂Na]·4CH₂Cl₂·Cl(CH₂)₂Cl (Tm = hydrido-trist(methimazolyl))borate, Tp = hydrido-tris(pyrazolyl)borate) [22], [HB(3-(C₂F₅)Pz)₃][Na(3-(C₂F₅)-PzH] [23], and Na₄[(Ph₃P)₆·6CH₃OH (Tp₆ = tris-3-phenyl-5-methyl-1,2,4-triazolyl)borate] [24]. Thus, the characterization of 2 constitutes a new example of a structurally characterized sodium tris(pyrazolyl)borate, in which the coordination of both Na atoms by three bridging molecules of acetone is unusual. To the best of our knowledge, only three structures exhibiting this mode of coordination were previously reported in the literature (based on a CDS query): [Na₃(Me₂CO)₁₂][Pb₄I₁₃(Me₂CO)] [25], [Na(Me₂CO)₉]n (I₂)ₙ [26] and [Na₄((Me₂CO)₁₅)[PbI₂I₁₂·3Me₂CO)] [27]. The three examples include exclusively polynuclear cations consisting of a collinear array of Na atoms. Therefore, the dinuclear (Me₂CO)₉Na₂ core revealed in 2 can be considered as unprecedented. A comparison of the Na–O bond lengths, the Na–Na distance, and the Na–O–Na angles with related compounds is given in Table 2.

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sented in the Supporting Information. Therefore, and according to the plausible Eq. 1, we assume that the unknown species could be related to the monoalkyldihydroxydistannate complexes, \([RSn(OH)(OH)\text{Cl}_2]\), reported in the past by Lecomte (\(R = \text{C}_2\text{H}_5\), [32]) and by Holmes (\(R = \text{C}_6\text{H}_5\), [33]).

\[
2\text{Tp}^\ast\text{Sn(Cl)}_2\text{Bu} + 2\text{NaOH} \rightarrow \text{MeCO/Me}_2\text{CO} \rightarrow ([\text{Me}_2\text{CO}]_3\text{NaTp}^\ast)_2 + [\text{BuSn(OH)(OH)Cl}_2]\]

(1)

Moreover, and according to the \(^{119}\text{Sn}\) NMR results achieved by Blunden, Smith and Gillies on the \(\text{H}_2\text{C}-\text{SnCl}_3-\text{D}_2\text{O}\) system [34], further substitution of chlorine atoms resulting in hydrolysis, can be plausibly expected. Thus, and still according to previous studies of Blunden [35], the tin species exhibiting a \(^{119}\text{Sn}\) \(^1\text{H}\) NMR chemical shift at \(-588\) ppm can be assigned to the inorganic salt \(\text{Na}_2\text{Sn(OH)}_6\). Further work is currently underway to extend the reported reaction and also to get a better understanding of the mechanism.

**Experimental Section**

The organic solvents were refluxed over appropriate desiccants, distilled and saturated with argon prior to use. Chemicals were purchased from Aldrich and Acros Organics. The reagents were used without further purification unless specified.

**Crystal structure determination**

A suitable single crystal of 2 was mounted on a mylar loop, and the diffraction data were collected at 115 K on a Bruker Nonius ApexII CCD equipped with a nitrogen jet stream low-temperature system (Oxford Cryosystems). The X-ray source was graphite-monochromatized MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å) from a sealed tube. Data were reduced by using the DENZO software without applying absorption corrections; the missing absorption corrections were partially compensated for by the data scaling procedure in the data reduction. Using OLEX2 [37], the structure was solved by the Charge Flipping method using the SUPERFLIP [38–40] program and refined with full-matrix least-squares on \(F^2\) using the SHELXL [41] program. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions and refined as riding atoms. Programs used for the representation of the molecular and crystal structures: ORTEP [42–44], DIAMOND [45].

**Supporting information**

The \(^1\text{H}\), \(^{13}\text{C}\) \(^1\text{H}\), \(^{11}\text{B}\) NMR spectra of 2, the \(^{119}\text{Sn}\) \(^1\text{H}\), \(^{11}\text{C}\) \(^{11}\text{H}\) NMR spectra assigned to tin co-products, and data on the X-ray solid-state structure determination of \(2\cdot\text{DCI}_3\) are shown in the Supporting Information (Figs. S1–S7, Tables S8–S14). This material is available online only (DOI: 10.5560/ZNB.2014-4066).

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