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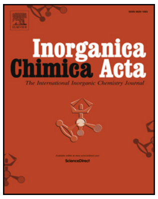

Research paper

The structure of four thallium tris(1*H*-pyrazol-1-yl)hydroborates in the solid state by X-ray crystallography and in solution by NMR and DFT-GIAO calculations

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ABSTRACT

The crystal and molecular structures of four thallium tris(1*H*-pyrazol-1-yl)hydroborates have been determined by X-ray analysis and compared with those recorded in the literature. The geometry of the pyrazole ring, steric effects of the substituents at position 3, packing and other characteristics of the crystals are discussed. Density Functional Theory-Gauge Invariant Atomic Orbital (DFT-GIAO) calculations have been carried out to determine the chemical shifts of the four compounds; they have been compared with experimental values finding an agreement excellent.

1. Introduction

Swiatoslaw (Jerry) Trofimenko introduced tris(1*H*-pyrazol-1-yl)hydroborates in 1966 and named them **scorpionates** [1–6]. Owing to our interest in pyrazoles [7–9], we collaborated with him on this and related topics [10–19] and simultaneously studied new scorpionates [20–22]. We have explored another field related to Trofimenko, that of the poly(1*H*-pyrazol-1-yl)methanes [23,24]. Scorpionates continue to be much studied as proven by a selection of papers published in 2016 [25–31], 2017 [32–35] and in 2018 [36–38].

In the present paper we will discuss the molecular and crystal structures of four thallium salts of scorpionates **1**–**4** (Scheme 1).

2. Experimental and computational details

2.1. Origin of the compounds

Compound **1** [tris(3-(4-methoxyphenyl)-1*H*-pyrazol-1-yl)hydroborate thallium salt], **2** [tris(3-(4-chlorophenyl)-1*H*-pyrazol-1-yl)hydroborate thallium salt] and **3** [tris(3-naphthalen-2-yl-1*H*-pyrazol-1-yl) hydroborate thallium salt] were reported in our paper, ref. [13]. Compound **4** [tris(3-cyclohexyl-1*H*-pyrazol-1-yl)hydroborate thallium salt] was described in refs. [13,16,39].

2.2. Single-crystal X-ray analysis

One suitable crystal of each compound was selected and collected on a Bruker APEX-II CCD diffractometer. The crystals were kept at room temperature during data collection except for compound **2** which it was cooled at 150 K with an Oxford Cryostream device. Using Olex2 [40], the structure of compound **1** was solved with ShelXS [41] and the structures of compounds **2**, **3** and **4** were solved with SIR2011 [42] structure solution programs using Direct Methods. All of them were refined with the ShelXL [43] refinement package using Least Squares minimization. Views of the four molecule structures with their atom labeling are depicted in Fig. 1 and Fig. 1S. A summary of the crystal data and structure refinement is included in Table 1S.

Compound **3** includes disordered solvent molecules that correspond to CH_2Cl_2 and $C_6H_5CH_3$ (see the NMR part). Note that a mixture of toluene and dichloromethane solvents was used in the crystallization experiment. However, although the residual electron density peaks reflected a more complex disordered model that probably includes low occupancy of dichloromethane molecules, a disorder model including this solvent could not be properly established and only toluene with full occupancy was modeled in two positions (Fig. 2S). Besides, it was necessary to introduce similarity restraints in the geometry and in the thermal parameters in order to refine the selected disordered model. Low-temperature data were also collected for compound **3**, but

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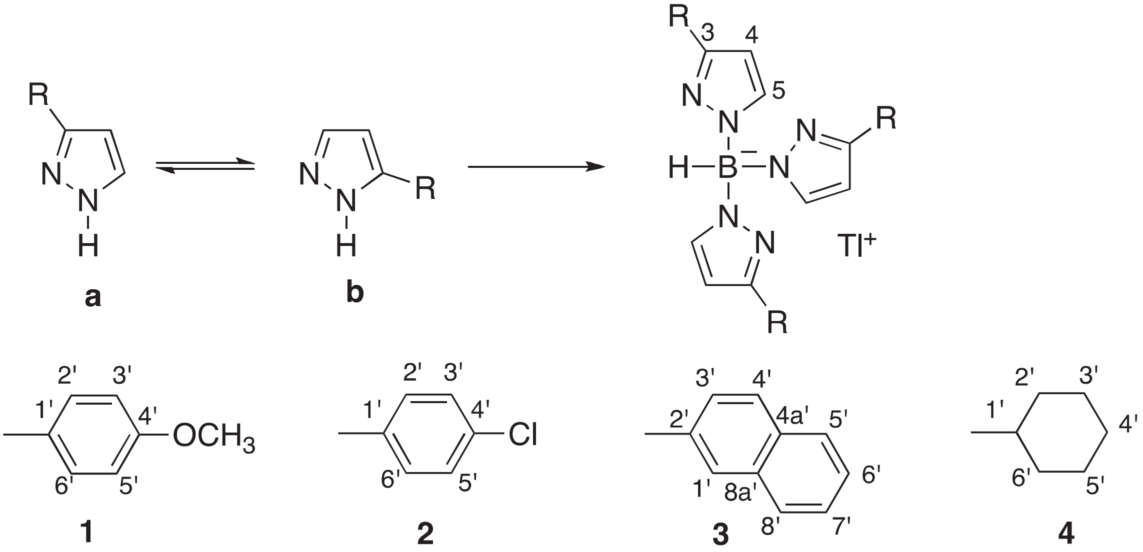

Scheme 1. Trispyrazolylhydroborates and the precursor pyrazoles with NMR atom numbering.

probably due to the fact that it was the second time that the same crystal was diffracted, the data significantly worsened, and the disorder problem did not improve. In order to obtain a different crystal structure that could prevent solvent disorder, we try to recrystallize compound **3** from other solvents. In those cases where suitable single crystals were obtained for X-ray diffraction experiment, the results showed that the title compound was decomposed, and only the corresponding NH-pyrazole (3-(naphthalen-2-yl)-1*H*-pyrazole) was observed. The structure of 3-(naphthalen-2-yl)-1*H*-pyrazole was reported in the CSD, refcode: MAFVOF [44].

2.3. Cambridge structural database

For comparison purposes a search of thallium tris(1*H*-pyrazol-1-yl) hydroborates, Tl[Tp], has been carried out in the Cambridge Structural Database (CSD, Version 5.39, updates to Feb 2018) [45]. Only the best R-factor structure has been kept when there are different hits for the same structure. Table 2S of the supplementary material contains the 62 retrieved structures from this search. These 62 structures contain 74 molecular fragments that have been included in our study.

2.4. Quantum chemical calculations

Chemical shifts have been theoretically calculated using an approach we have found yields excellent results. It consists in carrying out GIAO [46,47]/B3LYP [48,49]/6-311++G(d,p) [50,51] calculations to obtain absolute shieldings in the gas phase, then calculate them including the general solvation PCM model of Tomasi [52–54] for the desired NMR solvent (replacing D by H), in the case of the present work, $CHCl_3$ and DMSO. All these calculations were carried using the Gaussian 09 program [55]. Then we have transformed the absolute shieldings into chemical shifts by means of a series of empirical equations that we have devised for ^1H, ^{13}C and ^{15}N nuclei [56,57]. The geometry optimization starts from the experimental geometry, including the Tl atom, and then optimizes it to a C_3 symmetry because in solution NMR the three pyrazoles are equivalent. The results thus obtained are reported in Table 1. Although ^{15}N chemical shifts have not been reported we think it is useful to include them in Table 1.

3. Results and discussion

Four thallium tris(1*H*-pyrazol-1-yl)hydroborates have been determined by X-ray analysis and their molecular and crystal structure have been analyzed and compared with sixty-two Tl[Tp] derivatives recorded in the CSD.

Compounds **2** and **3** present a full thallium tris(1*H*-pyrazol-1-yl) hydroborate independent molecule ($Z' = 1$) in their structure as most of the Tl[Tp] compounds, Table 2. Molecules in compound **1** and **4** present a 3-fold axis and a mirror plane symmetry respectively; therefore only a third ($Z' = 1/3$) and a half ($Z' = 1/2$) of their molecule constitute the independent part. Among the sixty-two Tl[Tp] from the CSD, thirty-seven structures present one independent molecule and seven present more than one; the remaining eighteen structures contain molecules that present symmetry.

Table 3S shows a summary of the geometrical parameters of the four title molecules. Bond lengths and angles do not differ significantly among them and neither among similar fragments derived from the CSD, according to the information provided by the Mogul library [58]. Substituents on the pyrazole rings do not markedly distort the 6-membered rings formed by Tl, N1, N2 and B. Furthermore, the observed correlation between the Tl-N bond-length elongation and the N-Tl-N bond-angle decrease (Fig. 2) cannot be explained by the steric effect of the substituent at C3.

The three points off the distribution (marked with a red circle) correspond to structures that present three 7-*t*-butylindazole [59], 9-triptycylpyrazole [60] and 3-phenyl-4-cyanopyrazole [61] substituents on the boron atom. In the case of 7-*t*-butylindazole and 9-triptycylpyrazole this is due to the fact that they are very bulky; in the case of 3-phenyl-4-cyanopyrazole the anomaly can be explained because the thallium atoms present short distances (3.2 Å) to the nitrogen of the cyano groups at C4 of three adjacent Tp ligands, so they can be considered as 6-coordinated structures.

While pyrazole rings in compounds **1**, **2** and **3** present a dissymmetry in their internal angles reflecting the presence of 1*H*-pyrazole localized structure, in compound **4** the pyrazole rings reveals a more delocalized structure with C_{2v} symmetry (Table 3). Most of the sixty-two Tl[*Tp*]s present a dissymmetric pyrazole ring with average internal angles in N1 and N2 of 110(1)° and 106(2)° respectively. The ones that present C_{2v} symmetry correspond to scorpionates where indazol-1-yl