A One-Dimensional Thallium(I) Coordination Polymer Involving Polyhapto-Aromatic Interactions

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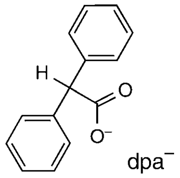
A one-dimensional coordination polymer involving Tl⋯C interactions, $[Tl(\mu_4\text{-dpa})]_n$(Hdpa = diphenylacetic acid), was synthesized and characterized. The single-crystal X-ray data of the compound show that the coordination number of the Tl^I ions is five and that Tl centers have an irregular coordination sphere containing a 'configurationally active' lone pair/hexahapto (η^6) interaction, thus resulting in a total hapticity of eleven for a TlC_6O_5 environment.

Introduction. – Thallium reagents, despite their inherent toxicity and cost, have played a conspicuous role in the development of modern inorganic and organometallic chemistry [1–5]. Thallium(I) chemistry is very interesting due to a variety of reasons: 1. thallium salts or complexes are often anhydrous; 2. the lone pair present at the Tl^I atom may or may not be 'configurationally active'; 3. the ability to exhibit a high coordination number because of the large size of the Tl^I ion; 4. the ease with which Tl^I complexes are able to form metal–metal bonds and also complexes with aromatic hydrocarbons [6–27]. In a recent structural study of Tl^I complexes of anthranilates and salicylates [8], it has been argued that polyhapto-aromatic interactions also play an important role in determining the solid-state lattices of such compounds. Thus it was anticipated that this might be true also for the Tl^I complex with the diphenylacetato ligand (Hdpa = diphenylacetic acid). The diphenylacetate anion is an interesting ligand with two aromatic groups, and because of its ability to form polyhapto complexes it may also be a very good candidate for the investigation of the 'configurational activity' of valence-shell electron lone pairs in polymeric and supramolecular compounds.

In the present study, the structure determination of the thallium(I) complex with dpa^- established the presence of a one-dimensional polymer which interestingly, involves new short Tl⋯C interactions.



Results and Discussion. – The reaction between diphenylacetic acid (Hdpa) and $Tl^I(NO_3)$ provided a crystalline material of the general formula $[Tl(\mu_4\text{-dpa})]_n$ (**1**). Determination of the structure of **1** by X-ray crystallography showed the complex to be a novel one-dimensional polymer (*Fig. 1,a*). There are five (TlO_5) coordinate Tl atoms, and the Tl centers can be considered to be five-coordinate. The separation between the Tl atoms is 4.223(7) Å, which is longer than the sum [8] of *van der Waals* radii of *ca.* 3.92 Å [8] of two Tl^I atoms. Hence, no thallophilic Tl–Tl interaction are considered for this compound. Each dpa^- ligand is pentadentate connecting four Tl^I ions. The COO^- group of the dpa^- ligand acts as both a bidentate chelating group where the two O-atoms of the COO^- group coordinate to a Tl^I ion, and as a bridging group where one of these O-atoms acts as a bridge to two other Tl^I atoms and the other O-atom is a bridge to only one Tl^I atom, a very novel and interesting behavior of a COO^- group (*Fig. 2*).

In **1**, the lone pair of Tl^I is 'active' in the solid state. However, the arrangement of the O-atoms suggests a gap or hole in the coordination sphere around the Tl^I atom (*Fig. 1*), a gap possibly occupied by a 'configurationally active' electron lone pair. Hence, the geometry of the coordination environment of every Tl^I atom is likely to be caused by the geometrical constraints of coordinated O-atoms, and by the influence of a 'configurationally active' electron lone pair in a hybrid orbital of the metal. The observed shortening of the Tl–O bond on the side of the Tl^I ion opposite to the putative lone pair (Tl–O(1) 2.687(6) Å compared with Tl–O(2) 2.831(5) Å adjacent to the lone pair) supports the presence of this feature [28].

To find any other potential donor center, it is necessary to extend the bonding limit. A search was made generally for Tl···C approaches, and it appears that the Tl center in **1** may also be involved in an η^6 interaction with the Ph groups of neighboring molecules. Thus, the Tl^I atoms are linked to 6 C-atoms of the Ph groups, with distances $Tl\cdots C(9)^i$, $Tl\cdots C(10)^i$, $Tl\cdots C(11)^i$, $Tl\cdots C(9)^{iii}$, $Tl\cdots C(13)^{iii}$ and $Tl\cdots C(14)^{iii}$ (*i*: $-y, x, -z$; *iii*: $-x, -y, z$) of 3.995(2), 3.561(2), 3.979(2), 3.824(3), 3.877(5), and 3.379(5) Å, respectively (*Figs. 1,b* and *3*). Hence, the Tl^I coordination sphere is completed, and rather than a TlO_5 coordination sphere, the complex can be considered to contain a hexahapto TlC_6O_5 center with an irregular eleven coordination number. In recently studied Tl species [8] [26], the Tl···C separations range from 3.20 to 4.00 Å. Thus, the hexahapto-aromatic coordination of the Tl^I atom appears to be yet another factor which can make varying contributions to the stability of the complexes of this metal ion. The obvious question then is whether the lone pair at the Tl^I atom is or is not involved in donor bonding. Since somewhat surprisingly, the very recent report of polyhapto-aromatic interactions in a Pb^{II} complex suggested that the active lone pair at the Pb^{II} atom may be involved in donor bonding [29]. Comparison of the structure data of **1** with those reported for the Pb^{II} compound suggests that the unusually high coordination number of **1** might reflect the capacity of Tl^I to act as both a *Lewis* acid and a *Lewis* base, like Pb^{II}.

There are edge-to-edge π–π stacking [30] [31] interactions between Ph groups of the dpa^- ligands belonging to adjacent chains of the coordination polymer in the network, with the distance 4.140 Å.

In summary, the structure of $[Tl(\mu_4\text{-dpa})]_n$ (**1**) is interesting because it represents a new, rarely observed one-dimensional framework with an unusual bridging of the COO^- group and with a hemisphere Tl^I coordination sphere. Moreover comparison

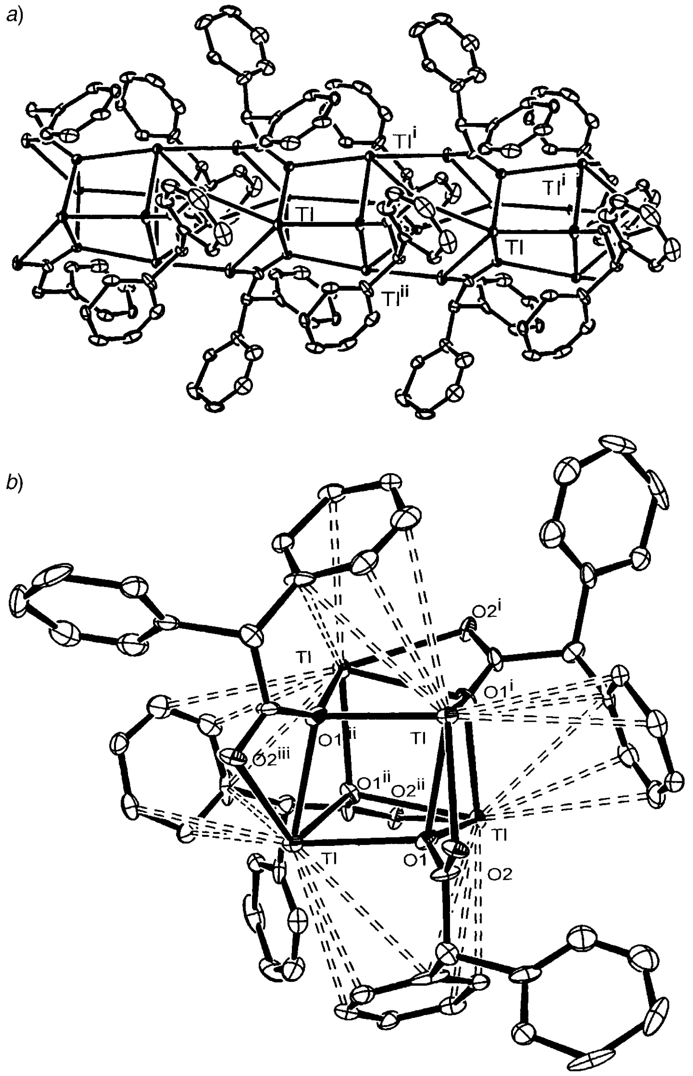


Fig. 1. a) *Fragment of the coordination polymer* **1** *showing the 1D pattern*; b) *bonding and polyhapto interactions within a fragment of the coordination polymer* **1** *after extending the bonding limit.* Selected bond lengths [Å]: Tl–O(1)^{i} 2.672(6), Tl–O(1) 2.687(6), Tl–O(1)^{ii} 2.828(5), Tl–O(2) 2.831(5), and Tl–O(2)^{iii} 2.874(5). Selected bond angles [°]: O(1)^{i}–Tl–O(1) 75.47(17), O(1)^{i}–Tl–O(1)^{ii} 78.32(18), O(1)–Tl–O(1)^{ii} 78.07(17), O(1)^{i}–Tl–O(2) 101.12(16), O(1)–Tl–O(2) 46.78(15), O(1)^{ii}–Tl–O(2) 121.31(15), O(1)^{i}–Tl–O(2)^{iii} 79.65(15), O(1)–Tl–O(2)^{iii} 105.78(17), O(1)^{ii}–Tl–O(2)^{iii} 155.84(16), and O(2)–Tl–O2^{iii} 72.79(16). Superscripts *i*, *ii*, and *iii* indicate the symmetry $(-y, x, -z)$, $(y, -x, -z)$, and $(-x, -y, z)$, respectively

with other reported complexes with O-donor ligands suggests the presence of an 'active' lone pair at the Tl^{I} ester of **1** which might be capped by involvement in a donor bonding and act as both a *Lewis* acid and a *Lewis* base.

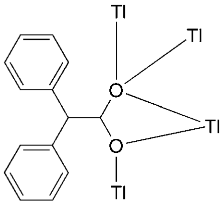


Fig. 2. *Line diagram of the coordination mode of the dpa$^-$ anion in the coordination polymer* **1**

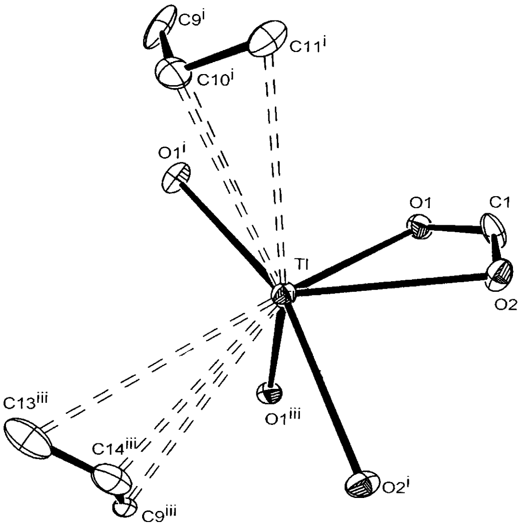


Fig. 3. *Tl···C Interactions within* **1** *after extending the bonding limit*

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Experimental Part

catena-*Poly[thallium-μ_4(diphenylacetato-κO,κO′:κO:κO:κO′)] (=(α-Phenylbenzeneacetato)thallium Homopolymer*; **1**) The complex [Tl(μ_4-dpa)]$_n$ was prepared by dissolving thallium(I) nitrate (0.266 g, 1 mmol) in distilled H_2O and MeOH and adding a mixture of diphenylacetic acid (0.212 g, 1 mmol) and NaOH (0.04 g, 1 mmol) in MeOH. The resulting soln. was stirred and then allowed to stand for some days at r.t. Slow evaporation of the solvent at r.t. yielded suitable crystals for X-ray analysis: 0.207g (50%) of **1**. The crystals were washed with acetone and air dried. M.p. 157°. IR (selected bands): 642*m*, 694*s*, 734*s*, 1361*s*, 1484*m*, 1532v*s*, 1563*s*, 1587*s*, 2885*w*, 3050*w*. Anal. calc. for $C_{14}H_{11}O_2Tl$: C 40.42, H 2.64, Tl 49.10; found: C 40.82, H 2.56, Tl 50.10.

X-Ray Crystal-Structure Analysis. Crystallographic measurements were made at 293(2) K with a *Bruker-Smart 1000-CCD* area detector [32]. The structure was solved and refined with the program system SHELXTL [33]. Intensity data were collected within the range $2.22° \leq \theta \leq 30.02°$ with graphite monochromated MoK_α radiation for a crystal of the dimension 0.25×0.12×0.04 mm. Plots were prepared with ORTEP III [34], and WinGX [35] was used as an interface during the structure-solution [36] procedure. Semiempirical absorption correction from equivalents was applied. Crystal data: formula, $C_{14}H_{11}O_2Tl$; M_r 415.60; tetragonal system, space group P-42(1)c; $a=b=18.3594(11)$, $c=7.3337(6)$ Å; $V=2472.0(3)$ Å^3; $D_c=2.233$ Mg/m^3 ($Z=8$); $F(000)=1536$; $R(wR)=0.0353$ (0.0803) for 3101 reflections, with $I>2\sigma(I)$; $R(wR)=0.0422$ (0.0828) for all data. The absolute structure of the noncentrosymmetric was determined by refinement of *Flack*'s parameter $x=-0.040(18)$ [37].

CCDC-270822 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* http://www.ccdc.cam.ac.uk/data_request/cif.

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